

Supplementary Information

A Novel Metal- and Mineral-acid free Synthesis of Organic Ammonium Tribromides and Application of Ethylenepheneanthrolium Bistribromide for Bromination of Active Methylene Group of 1, 3-Diketones and β -Ketoesters

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General Information All the reagents (chemicals and solvents) were purchased commercially and used without further purification. The synthesized tribromides and other monobrominated products were characterized with UV-Vis, FT-IR and NMR (^1H & ^{13}C) spectroscopy. Elemental analysis was done by FLASH EA 1112 series. Bromine from QATBs and EPDBT was estimated by chemical method.¹ UV-Vis spectra were taken in MeCN medium with Carry Varian-450 UV-Vis spectrophotometer. FT-IR spectra were recorded in KBr or neat with MAGNA 550 FT-IR spectrometer. ^1H and ^{13}C Nuclear Magnetic Resonance spectra of pure compounds were acquired at 500 MHz with CDCl_3 as the internal standards.

Representative Procedures

1. Synthesis of EPDBT: Firstly, 1,10-(ethane-1,2-diyl)phenanthroline dication dibromide was prepared by refluxing phenanthroline (10 mmol, 1.96 g) and 1,2-dibromoethane (10 mmol, 1 mL) in acetone (6 mL) in a RB for 0.5 h at temperature of 90°C . The solid product of dibromide precipitated was filtered, followed by washing with Et_2O (2 X 10 mL), dried in vacuum and then recrystallized from EtOH-water (2:5) mixture.

Now 1 equiv of dibromide (1 mmol, 0.354 g), thus prepared, 4 equiv of KBr (4 mmol, 0.476 g) and 4 eq. of MCPBA (4 mmol, 0.692 g) were mixed in 10 mL of water and stirred for *ca.* 5 min. The orange coloured product formed was washed with NaHCO_3 solution (10 %) for several times to remove unreacted MCPBA. After that the crude product was again washed with water to remove by-products. The compound was dried *in vacuo* and recrystallized with EtOAc. Yield: 0.610 g; 90 %.

2. Synthesis of tetramethyl ammonium tribromide, TMATB: 1 equiv of tetramethyl ammonium bromide (1 mmol, 0.154 g), 2 equiv of KBr (2 mmol, 0.238 g) and 2 equiv of MCPBA (2 mmol, 0.346 g) were mixed together in 10 mL of water and stirred for *ca.* 2 min. The orange coloured product formed was washed with NaHCO_3 solution (10 % solution) for several times to remove unreacted substrate. After that the crude product was again washed with water to remove by-products. The compound was dried *in vacuo* and recrystallized with EtOAc; mp: 117°C . Yield: 0.284 g; 93 %.

3. Synthesis of tetraethyl ammonium tribromide, TEATB: 1 equiv of tetraethyl ammonium bromide (1 mmol, 0.210 g), 2 equiv of KBr (2 mmol, 0.238 g) and 2 equiv of MCPBA (2 mmol, 0.346 g) were mixed together in 10 mL of water and stirred for *ca.* 3 min. The orange coloured product formed was washed with NaHCO₃ solution (10 % solution) for several times to remove unreacted substrate. After that the crude product was again washed with water to remove by-products. The compound was dried *in vacuo* and recrystallized with EtOAc; mp: 87°C. Yield: 0.340 g; 92 %.

4. Synthesis of tetrabutyl ammonium tribromide, TBATB: 1 equiv of tetrabutyl ammonium bromide (1 mmol, 0.322 g), 2 equiv of KBr (2 mmol, 0.238 g) and 2 equiv of MCPBA (2 mmol, 0.346 g) were mixed together in 10 mL of water and stirred for *ca.* 5 min. The orange coloured product formed was washed with NaHCO₃ solution (10 % solution) for several times to remove unreacted substrate. After that the crude product was again washed with water to remove by-products. The compound was dried *in vacuo* and recrystallized with EtOAc; mp: 75°C. Yield: 0.462 g; 96 %.

5. Synthesis of cetyltrimethyl ammonium tribromide, CTMTB: 1 equiv of cetyltrimethyl ammonium bromide (1 mmol, 0.364 g), 2 equiv of KBr (2 mmol, 0.238 g) and 2 equiv of MCPBA (2 mmol, 0.346 g) were mixed together in 10 mL of water and stirred for *ca.* 6 min. The orange coloured product formed was washed with NaHCO₃ solution (10 % solution) for several times to remove unreacted substrate. After that the crude product was again washed with water to remove by-products. The compound was dried *in vacuo* and recrystallized with EtOAc; mp: 90°C. Yield: 0.439 g; 90 %.

6. Synthesis of Benzyltrimethylammonium tribromides, BTMATB: 1 equiv of benzyltrimethyl ammonium bromide (1 mmol, 0.120 g), 2 equiv of KBr (2 mmol, 0.238 g) and 2 equiv of MCPBA (2 mmol, 0.346 g) were mixed together in 10 mL of water and stirred for *ca.* 6 min. The orange coloured product formed was washed with NaHCO₃ solution (10 % solution) for several times to remove unreacted substrate. After that the crude product was again washed with water to remove by-products. The compound was dried *in vacuo* and recrystallized with EtOAc; mp: 99°C. Yield: 0.346 g; 89 %.

Procedure for monobromination at active methylene group of 1, 3-diketones and β -ketoesters

1. Preparation of methy-2-bromol-3-oxobutanoate (1b): 0.6 mmol of EPDTB (0.818 g) was dissolved in 5 mL of EtOAc followed by the addition of 1 mmol of methyl-3-oxobutanoate (~ 0.1 mL) to the solution. The reaction mixture was stirred maintaining cool condition (5-10°C) in a magnetic stirrer for *ca.* 25 min until the solution becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The organic layer was dried over anhyd Na_2SO_4 after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude product.

2. Preparation of ethyl-2-bromo-3-oxobutanoate (2b): 0.6 mmol of EPDTB (0.818 g) was dissolved in 5 mL of EtOAc followed by the addition of 1 mmol of ethyl-3-oxobutanoate (~ 0.1 mL) to the solution. The reaction mixture was stirred maintaining cool condition (5-10°C) in a magnetic stirrer for *ca.* 24 min until the solution becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The organic layer was dried over anhyd Na_2SO_4 after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude brominated product.

3. Preparation of 3-bromo-2, 4-pentanedione (3b): 0.6 mmol of EPDTB (0.818 g) was dissolved in 5 mL of EtOAc followed by the addition of 1 mmol of pentane-2,4-dione (0.1 mL) to the solution. The reaction mixture was stirred maintaining cool condition (5-10°C) in a magnetic stirrer for *ca.* 17 min until the solution becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The organic layer was dried over anhyd Na_2SO_4 after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude product.

4. Preparation of 2-methyl-2-propenyl-2-bromo-3-oxobutanoate (4b): 0.6 mmol of EPDTB (0.818 g) was dissolved in 5 mL of EtOAc followed by the addition of 1 mmol of t-butyl-3-oxobutanoate (0.16 mL)

to the solution. The reaction mixture was stirred maintaining cool condition (5-10°C) in a magnetic stirrer for *ca.* 27 min until the solution becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The organic layer was dried over anhyd Na₂SO₄ after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude product.

5. Preparation of 2-bromo-1-phenylbutane-1, 3-dione (5b): 0.6 mmol of EPDTB (0.818 g) and 1 mmol of 1-phenylbutane-1,3-dione (0.162 g) were dissolved in 5 mL of EtOAc. The resultant mixture was stirred maintaining cool condition (5-10°C) in a magnetic stirrer for *ca.* 14 min until the solution becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The organic layer was dried over anhyd Na₂SO₄ after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude liquid product.

6. Preparation of 2-bromoethyl-3-oxo-3-phenylpropanoate (6b): 0.6 mmol of EPDTB (0.818 g) was dissolved in 5 mL of EtOAc followed by the addition of 1 mmol of ethyl-3-oxo-3-phenylpropanoate (0.17 mL) to the solution. The reaction mixture was stirred maintaining cool condition (5-10°C) in a magnetic stirrer for *ca.* 29 min until the solution becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The organic layer was dried over anhyd Na₂SO₄ after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude product.

7. Preparation of 2-bromo-1, 3-diphenylpropane-1, 3-dione (7b): 0.6 mmol of EPDTB (0.818 g) and 1 mmol of 1, 3-diphenylpropane-1,3-dione (0.224 g) were dissolved in 8 mL of EtOAc. The resultant mixture was stirred maintaining cool condition (5-10°C) in a magnetic stirrer for *ca.* 15 min until the solution becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The

organic layer was dried over anhyd Na_2SO_4 after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude liquid product.

8. Preparation of 2-bromo-2-methylcyclohexane-1, 3-dione (8b): 0.6 mmol of EPDTB (0.818 g) was dissolved in 5 mL of EtOAc followed by the addition of 1 mmol of methylcyclohexane-1, 3-dione (~ 0.1 mL) to the solution. The reaction mixture was stirred maintaining cool condition (5-10°C) in a magnetic stirrer for *ca.* 19 min until the solution becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The organic layer was dried over anhyd Na_2SO_4 after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude product.

9. Preparation of 2-bromobenzyl-3-oxobutanoate (9b): 0.6 mmol of EPDTB (0.818 g) was dissolved in 5 mL of EtOAc followed by the addition of 1 mmol of benzyl-3-oxobutanoate (0.2 mL) to the solution. The reaction mixture was stirred maintaining cool condition (5-10°C) in a magnetic stirrer for *ca.* 26 min until the solution becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The organic layer was dried over anhyd Na_2SO_4 after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude product.

10. Preparation of 2-bromo-5, 5-dimethylcyclohexane-1, 3-dione (10b): 0.6 mmol of EPDTB (0.818 g) and 1 mmol of 5,5-dimethylcyclohexane-1,3-dione (0.140 g) were dissolved in 5 mL of EtOAc. The resultant mixture was stirred maintaining cool condition (5-10°C) in a magnetic stirrer for *ca.* 20 min until the solution becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The organic layer was dried over anhyd Na_2SO_4 after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude liquid product.

11. Preparation of 2-acetyl-2-bromocyclohexanone (11b): 0.6 mmol of EPDTB (0.818 g) and 1 mmol of 2-acetylcyclohexanone (0.130 mL) were dissolved in 5 mL of EtOAc. The resultant mixture was stirred maintaining cool condition (5-10°C) in a magnetic stirrer for *ca.* 19 min until the solution becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The organic layer was dried over anhyd Na₂SO₄ after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude liquid product.

12. Preparation of 1-bromo-2-oxocyclohexanecarboxylic acid ethyl ester (12b): 0.6 mmol of EPDTB (0.818 g) and 1 mmol of 2-oxocyclohexanecarboxylic acid ethyl ester (0.160 mL) were dissolved in 5 mL of EtOAc. The resultant mixture was stirred maintaining cool condition (5-10°C) in a magnetic stirrer for *ca.* 27 min until the solution becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The organic layer was dried over anhyd Na₂SO₄ after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude liquid product.

13. Preparation of 2-bromo-4, 4-dimethyl-1-phenylpentane-1, 3-dione (13b): 0.6 mmol of EPDTB (0.818 g) and 1 mmol of 4, 4-dimethyl-1-phenylpentane-1, 3-dione (0.237 mL) were dissolved in 5 mL of EtOAc. The resultant mixture was stirred maintaining cool condition (5-10°C) in a magnetic stirrer for *ca.* 16 min until the solution becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The organic layer was dried over anhyd Na₂SO₄ after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude liquid product.

14. Preparation of 2-bromo-(1-*p*-tolyl) butane-1, 3-dione (14b): 0.6 mmol of EPDTB (0.818 g) and 1 mmol of 1-*p*-tolylbutane-1, 3-dione (0.164 mL) were dissolved in 5 mL of EtOAc. The resultant mixture was stirred maintaining cool condition (5-10°C) in a magnetic stirrer for *ca.* 15 min until the solution

becomes colourless. The progress of the reaction was monitored by doing TLC (10 % EtOAc/hexane). After the completion of reaction, the mixture was washed with water (2 X 5 mL). The organic layer was dried over anhyd Na_2SO_4 after separating from aq layer. The excess solvent was removed by evaporation in a rotary evaporator to get the crude liquid product.

Spectral Data of OATBs

TMATB²: Orange compd; mp 117°C; Yield: 93% (0.284 g); UV-Vis: 271 nm; Anal., $\text{C}_4\text{H}_{12}\text{NBr}_3$ (Mol Wt 313.81): Calcd C 15.30, H 3.85, N 4.46, Br 76.37; Found C 15.32, H 3.57, N 4.54, Br 76.02.

TEATB²: Orange compd; mp 87°C; Yield: 92% (0.340 g); UV-Vis: 270 nm; Anal., C₈H₂₀NBr₃ (Mol Wt 369.918): Calcd C 25.97, H 5.44, N 3.78 Br 76.37; Found C 26.02, H 5.58, N 3.64, Br 76.17.

TBATB³: Orange compd; mp 75°C; Yield: 96% (0.462 g); UV-Vis: 267 nm; Anal., C₁₆H₃₆NBr₃ (Mol Wt 482.134): Calcd C 39.86, H 7.51, N 2.90, Br 76.37; Found C 39.72, H 7.58, N 2.54, Br 76.40.

CTMATB^{2,3}: Orange compd; mp 90°C; Yield: 90% (0.439 g); UV-Vis: 268 nm; Anal., C₁₉H₄₂NBr₃ (Mol Wt 524.215): Calcd C 43.53, H 8.08, N 2.67, Br 76.37; Found C 43.59, H 8.28, N 2.64, Br 76.22.

BTMATB⁴: Orange compd; mp 99°C; Yield: 89% (0.346 g); UV-Vis: 279 nm; Anal., C₁₀H₁₆NBr₃ (Mol Wt 390.60): Calcd C 30.80, H 4.13, N 3.59, Br 76.37; Found C 30.89, H 4.28, N 3.64, Br 76.15.

Spectral Data of Brominated Products:

Methyl 2-bromo-3-oxobutanoate⁵ (**1b**): Oily liquid; bp 215°C; Yield: 96 %; FT-IR: 3493, 2986, 1792, 1718, 869 cm⁻¹; ¹H NMR δ : 4.19 (s, 1H), 3.07 (s, 3H), 2.18 (s, 3H); ¹³C NMR δ : 27, 51, 67, 164, 201; Anal., C₅H₇O₃Br (Mol Wt 195.01): Calcd C 30.79, H 3.62; Found C 30.73, H 3.58.

Ethyl 2-bromo-3-oxobutanoate⁶ (**2b**): Liquid; bp 230-232°C; Yield: 89 %; FT-IR: 1745, 1718 cm⁻¹; ¹H NMR δ : 4.70 (s, 1H), 3.38 (q, J = 7.1 Hz, 2H), 2.45 (t, J = 7.1 Hz, 3H), 1.27 (s, 3H); ¹³C NMR δ : 15, 26.3, 55, 67, 163, 198; Anal., C₆H₉O₃Br (Mol Wt 209.03): Calcd C 34.47, H 4.34; Found C 34.50, H 4.37.

3-Bromopentane-2,4-dione⁷ (**3b**): Liquid; Yield: 88 %; FT-IR: 1743, 1721 cm⁻¹; ¹H NMR δ : 4.17 (s, 6H), 2.07 (s, 1H); ¹³C NMR δ : 27, 67, 195; Anal., C₅H₇O₂Br (Mol Wt 179.01): Calcd C 33.52, H 3.94; Found C 33.47, H 3.90.

***t*-Butyl 2-Bromo-3-oxobutanoate**⁸ (**4b**): Liquid; bp 240°C; Yield: 92 %; FT-IR: 1732, 1718 cm⁻¹; ¹H NMR δ : 4.10 (s, 1H), 2.02 (s, 3H), 1.23 (s, 9H); ¹³C NMR δ : 27, 31, 67, 84, 164, 206; Anal., C₈H₁₃O₃Br (Mol Wt 237.09): Calcd C 40.53, H 5.53; Found C 40.41, H 5.57.

2-Bromo-1-phenylbutane-1,3-dione⁹ (5b): Solid; mp 30-31°C (lit. mp 31-32°C); Yield: 80 %; FT-IR (KBr): 2964, 1710, 1622, 1418, 966, 780 cm⁻¹; ¹H NMR δ : 7.99, 7.42-7.70 (m, 4H), 5.60 (s, 1H), 2.52 (s, 3H); ¹³C NMR δ : 30, 70, 128, 130, 133, 140, 196, 210; Anal., C₁₀H₉O₂Br (Mol Wt 241.076): Calcd C 49.82, H 3.76; Found C 49.73, H 3.70.

Ethyl 2-bromo-3-oxo-3-phenylpropanoate¹⁰ (6b): Colourless oil; Yield: 82 %; FT-IR: 2990, 1759, 1687, 1344, 1025, 678 cm⁻¹; ¹H NMR δ : 7.98 (d, J = 8.1 Hz, 2H), 7.60 (t, J = 8.1 Hz, 1H), 7.48 (t, J = 8.1 Hz, 2H), 5.56 (s, 1H), 4.28 (q, J = 8.1 Hz, 2H), 1.27 (t, J = 8.1, 3H); ¹³C NMR δ : 14, 46, 64, 129, 131, 134, 167, 190; Anal., C₁₁H₁₁O₃Br (Mol Wt 271.102): Calcd C 48.73, H 4.09; Found C 48.67, H 3.99.

2-Bromo-1,3-diphenylpropane-1,3-dione¹¹ (7b): Colourless crystals; mp 90-91°C (lit. mp 89-92°C); Yield: 85 %; FT-IR (KBr): 1690, 1598, 1447, 995, 686 cm⁻¹; ¹H NMR δ : 7.87 (d, J = 7.2 Hz, 4H), 7.57 (t, J = 7.2 Hz, 2H), 7.42 (t, J = 7.2 Hz, 4H), 6.60 (s, 1H); ¹³C NMR δ : 93, 127, 129, 136, 186; Anal., C₁₅H₁₁O₂Br (Mol Wt 303.142): Calcd C 59.43, H 3.66; Found C 59.50, H 3.68.

2-Bromo-2-methylcyclohexane-1,3-dione¹⁰ (8b): Liquid; bp 64-65°C (lit. bp 65-66°C); Yield: 86 %; ¹H NMR δ : 1.65-1.88 (m, 1H), 1.80 (s, 3H), 2.20-2.35 (m, 1H), 2.58 (dt, J = 18.1 Hz, 7.5, 2H), 3.35 (ddd, J = 18.1 Hz, 11.7 Hz, 7.5 Hz, 2H); ¹³C NMR δ : 16.5, 19.2, 36, 79, 203; Anal., C₇H₉O₂Br (Mol Wt 189.046): Calcd C 44.47, H 4.80; Found C 44.32, H 4.71.

Benzyl 2-bromo-3-oxobutanoate⁸ (9b): Oily liquid; Yield: 92 %; ¹H NMR δ : 7.29-7.42 (m, 5H), 5.30 (s, 1H), 4.81 (s, 3H), 2.40 (s, 3H); ¹³C NMR δ : 28, 50, 69, 127.9, 128.3, 128.5, 140.1, 180, 196; Anal., C₁₁H₁₁O₃Br (Mol Wt 271.102): Calcd C 48.73, H 4.09; Found C 48.80, H 4.01.

2-Bromodimedone⁸ (10b): Solid; mp 157-159°C (lit. mp 156°C); Yield: 80 %; FT-IR (KBr): 1678, 1440, 1327 cm⁻¹; ¹H NMR δ : 6.40 (s, 1H), 2.52 (s, 2H), 2.43 (s, 2H), 1.12 (s, 6H); ¹³C NMR δ : 24.5, 40.8, 42.5, 51.1, 98.7, 191.1, 193; Anal., C₈H₁₁O₂Br (Mol Wt 219.072): Calcd C 43.83, H 5.06; Found C 43.90, H 5.19.

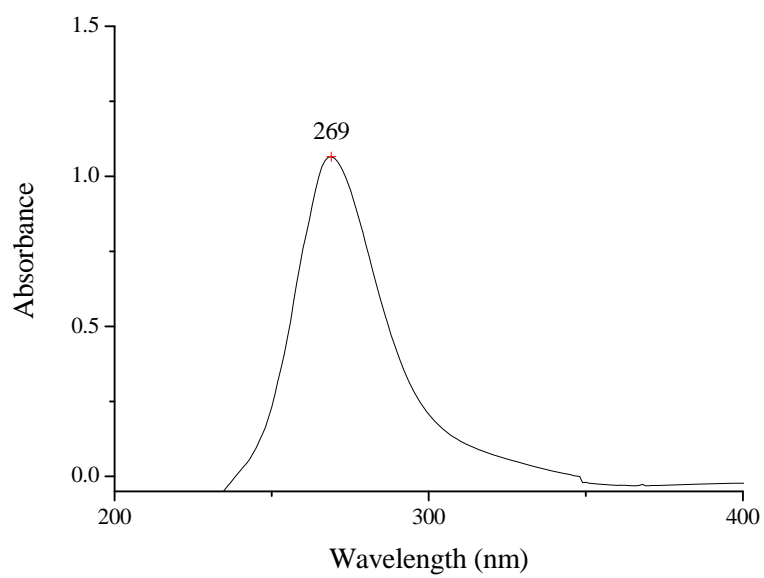
2-Acetyl-2-bromocyclohexanone¹⁰ (11b): Oily product; Yield: 81 %; FT-IR: 2940, 2880, 1712, 1212, 1120, 1073, 913 cm^{-1} . ^1H NMR δ : 3.10-3.20 (m, 1H), 2.50-2.68 (m, 1H), 2.30 (s, 3H), 2.29-2.45 (m, 1H), 2.16-2.29 (m, 1H), 1.91-2.07 (m, 2H), 1.70-1.85 (m, 2H); ^{13}C NMR δ : 20, 23.8, 24.6, 35.3, 36.7, 207.1, 208.2; Anal., $\text{C}_8\text{H}_{11}\text{O}_2\text{Br}$ (Mol Wt 219.072): Calcd C 43.86, H 5.06; Found C 43.09, H 4.98.

1-Bromo-2-oxo-cyclohexanecarboxylic Acid Ethyl Ester¹² (12b): Oily product; Yield: 85 %; FT-IR: 2981, 1755, 1725, 1625, 1252, 1022, 858, 784, 735 cm^{-1} ; ^1H NMR δ : 1.30 (t, $J = 7.0$ Hz, 3H), 1.75-1.82 (m, 2H), 1.87-1.92 (m, 2H), 2.17-2.21 (m, 1H), 2.37-2.50 (m, 2H), 2.72-2.82 (m, 1H), 4.28 (q, $J = 7.0$, 2H); Anal., $\text{C}_9\text{H}_{13}\text{O}_3\text{Br}$ (Mol Wt 249.098): Calcd C 43.40, H 5.26; Found C 43.56, H 5.38.

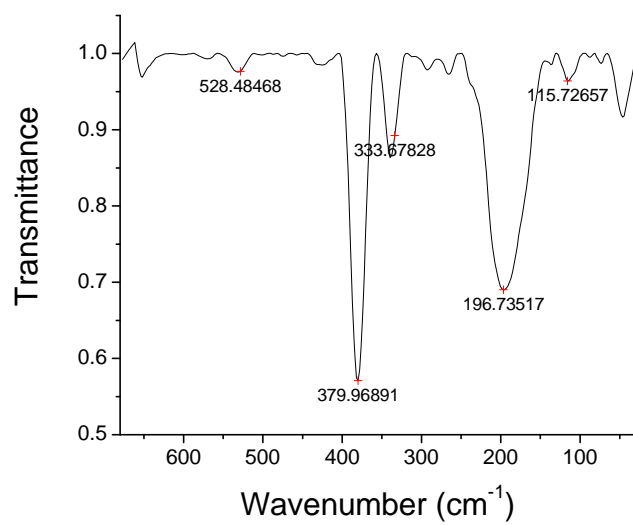
2-Bromo-1-*t*-butyl-3-phenylpropane-1,3-dione (13b): Oily product; Yield: 81%; FT-IR (Neat): 1736, 1742 cm^{-1} ; ^1H NMR δ : 7.91-7.87 (m, 2H), 7.52 (tt, $J = 7.5$ Hz, 1.5 Hz, 1H), 7.47-7.44 (m, 2H), 6.31 (s, 1H), 1.26 (s, 9H); ^{13}C NMR δ : 27.4, 40, 92.1, 127, 129, 132.1, 136, 185, 202.1; Anal., $\text{C}_{13}\text{H}_{15}\text{O}_2\text{Br}$ (Mol Wt 283.15): Calcd C 55.14, H 5.34; Found C 55.02, H 5.19.

2-Bromo-1-methyl-3-(4-methoxy)phenylpropane-1,3-dione (14b): Yellow oil; Yield: 80 %; ^1H NMR δ : 7.80 (d, $J = 8.5$, 2H), 7.25 (d, $J = 8.5$, 2H), 6.18 (s, 1H), 2.42 (s, 3H), 2.20 (s, 3H); ^{13}C NMR δ : 22, 55.4, 95.8, 113.9, 129.1, 131.1, 163.1, 184.1, 191.6; Anal., $\text{C}_{11}\text{H}_{11}\text{O}_2\text{Br}$ (Mol Wt 255.102): Calcd C 51.79, H 4.35; Found C 51.65, H 4.20.

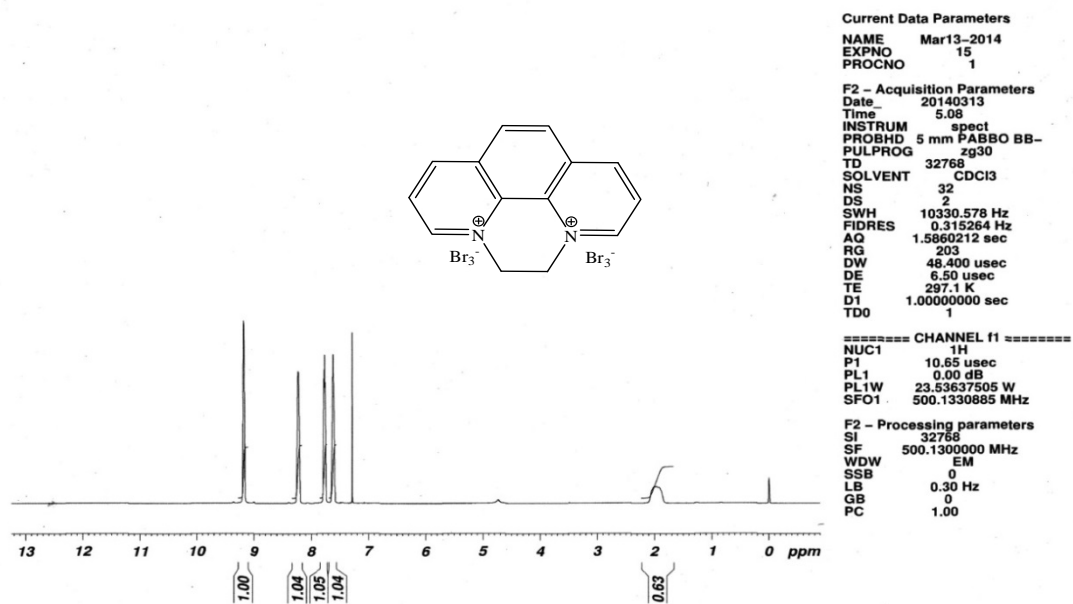
List of Spectra



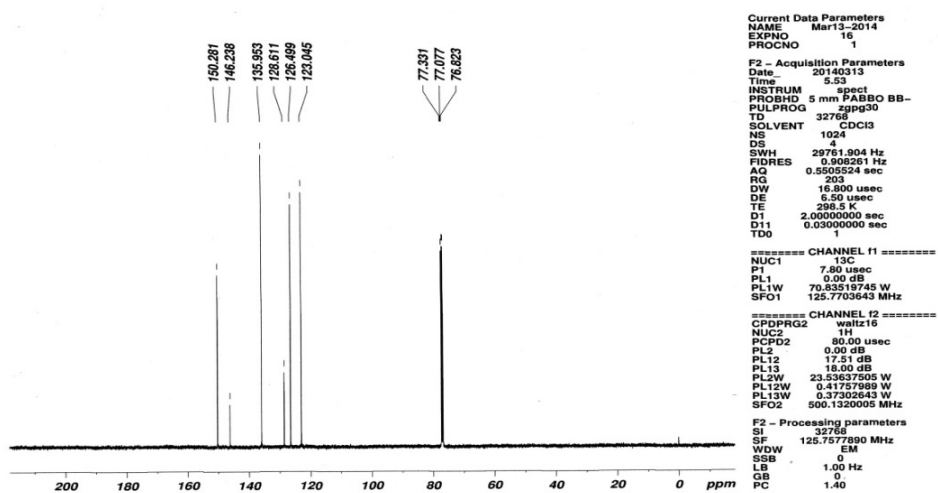
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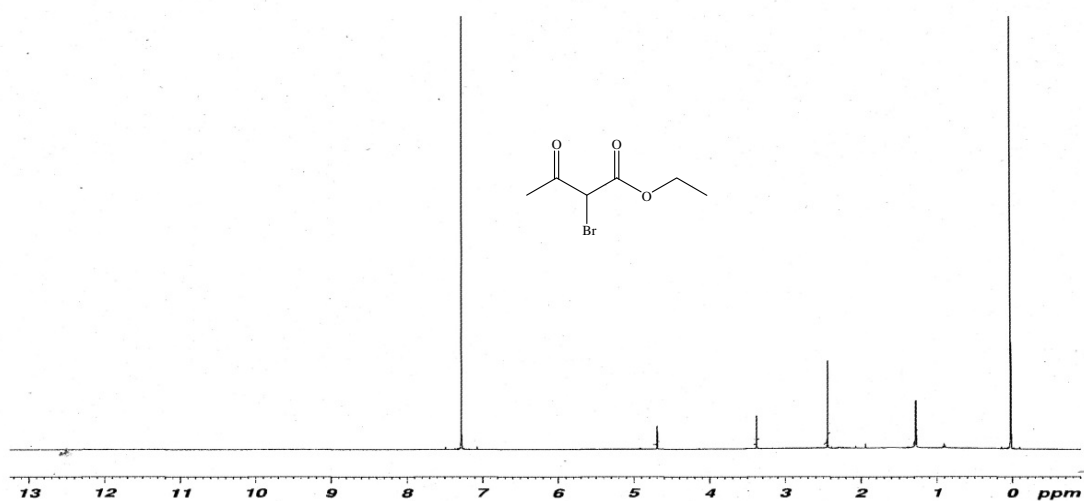
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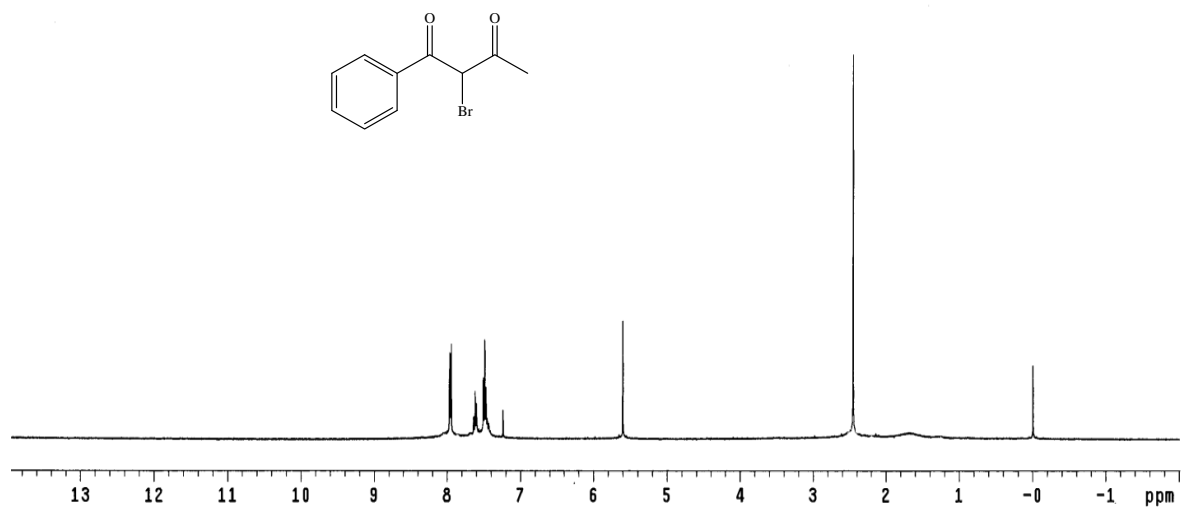
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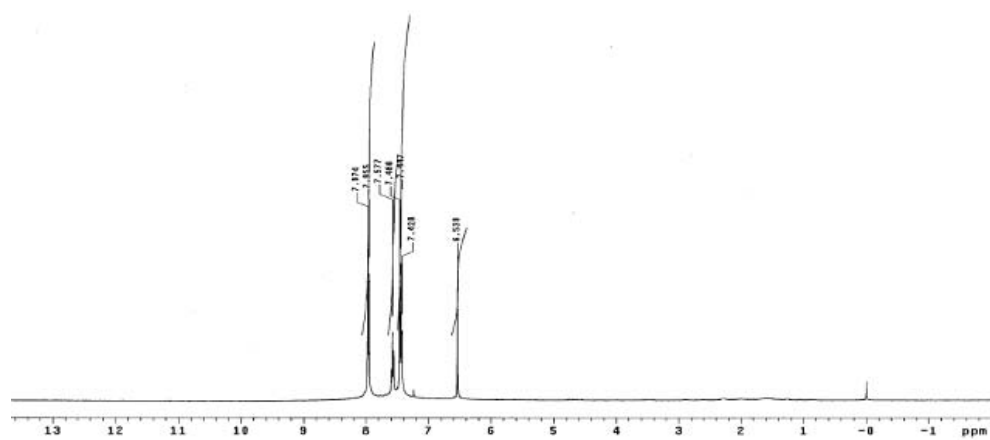
¹H NMR Spectrum of Compd 2b (S5)

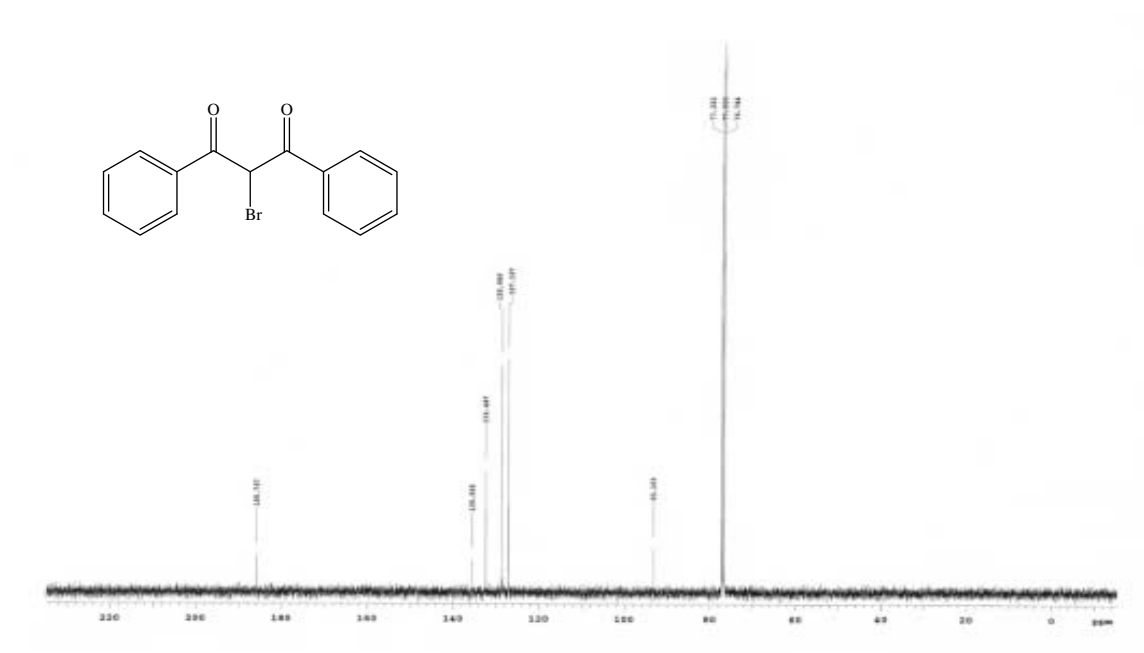
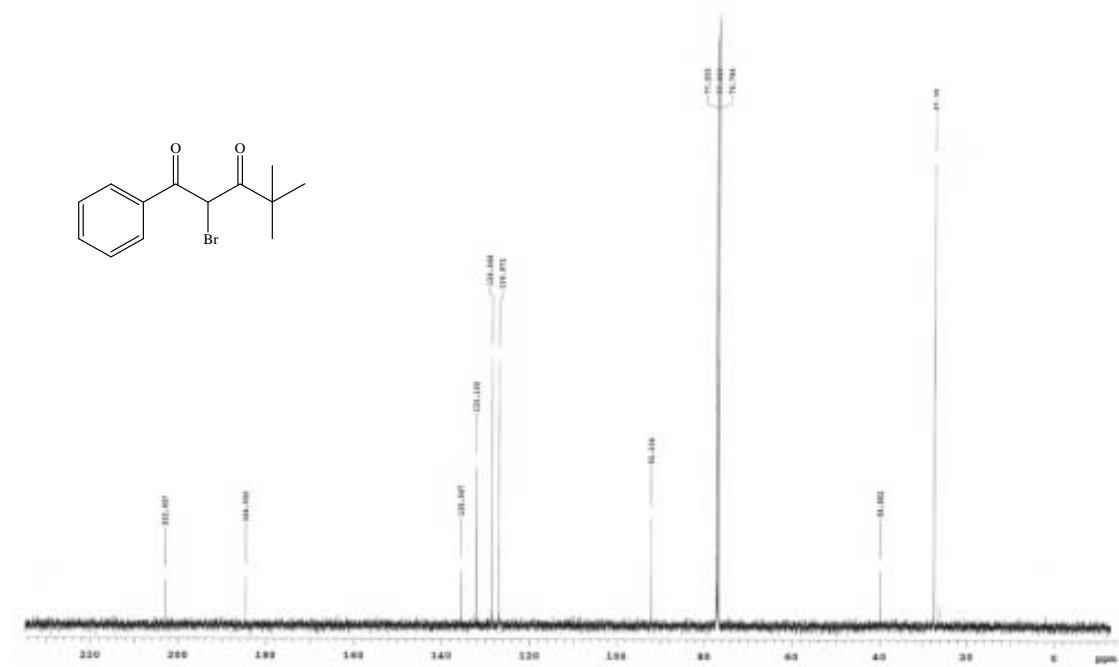


¹H NMR Spectrum of Compd 5b (S6)

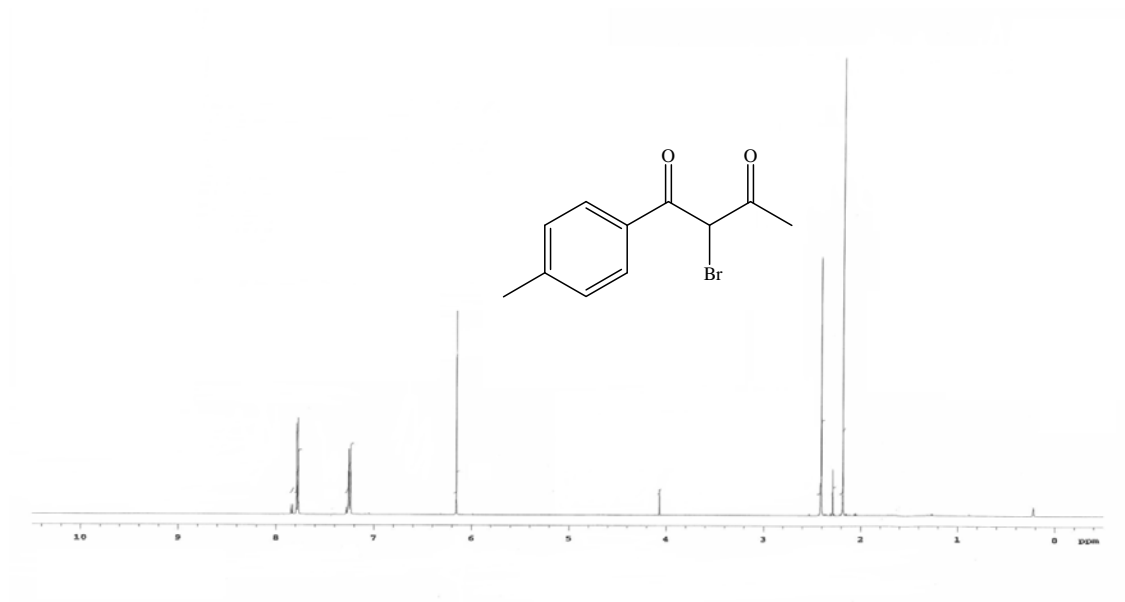


¹H spectrum of 7b (S7)

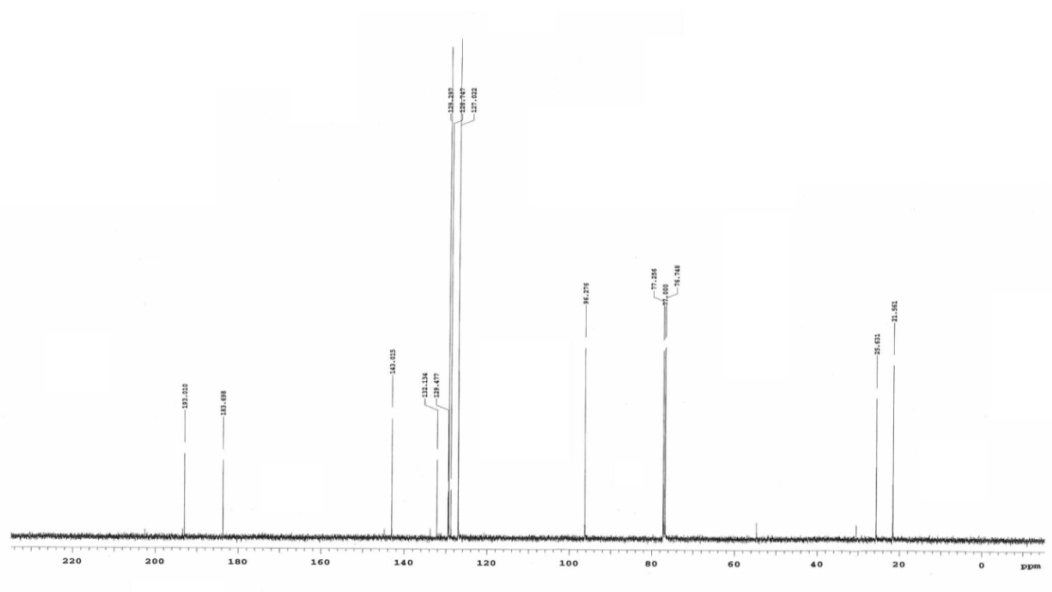


^{13}C NMR spectrum of 7b (S8)¹³C NMR Spectrum of 13b (S9)

^1H Spectrum of 14b (**S10**)



^{13}C NMR spectrum of 14b (**S11**)



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