SOLID PHASE BENZOYLATION OF PHENOLS AND ALCOHOLS IN MICROWAVE REACTOR: AN ECO-FRIENDLY PROTOCOL

SUPPLEMENTAL MATERIAL

Suchandra Chakraborty^{1*}, Ahana Saha,¹ Kaushik Basu² and Chandan Saha¹

¹*Department of Clinical and Experimental Pharmacology, School of Tropical Medicine, 108, Chittaranjan Avenue, Kolkata – 700073, India.*

²*Department of Chemistry, St Paul's Cathedral Mission College, Kolkata 700009.*

Table of contents	Page No.
1. General procedure for benzylation of phenol	S3
2. General procedure for 3,5-dinitrobenzylation of alcohols/ phenols	S3
3. Characteristics Spectral data for the representative benzoates	S4-S8
4. References	S8-S9
5. Figure S1. Method Set up for the benzylation of phenol in microwave reactor	S10
6. Figure S2. Graph of the progress of the reaction	S10
7. Figure S3. ¹ H-NMR spectra of 2,3-dimethylphenyl benzoate (2d)	S11
8. Figure S4. ¹³ C-NMR spectra of 2,3-dimethylphenyl benzoate (2d)	S11
9. Figure S5. ¹ H-NMR spectra of 2-isopropyl-5-methylphenyl benzoate (2f)	S12
10. Figure S6. ¹³ C-NMR spectra of 2-isopropyl-5-methylphenyl benzoate (2f)	S12
11. Figure S7. ¹ H-NMR spectra of 4-chlorophenyl benzoate (2h)	S13
12. Figure S8. ¹³ C-NMR spectra of 4-chlorophenyl benzoate (2h)	S13
13. Figure S9. ¹ H-NMR spectra of 1,4-phenylene dibenzoate (2k)	S14
14. Figure S10. ¹³ C-NMR spectra of 1,4-phenylene dibenzoate (2k)	S14
15. Figure S11. ¹ H-NMR spectra of 2-formylphenyl benzoate (2l)	S15
16. Figure S12. ¹³ C-NMR spectra of 2-formylphenyl benzoate (2l)	S15
17. Figure S13. ¹ H-NMR spectra of 4-formyl-2-methoxyphenyl benzoate (2n)	S16
18. Figure S14. ¹³ C-NMR spectra of 4-formyl-2-methoxyphenyl benzoate (2n)	S16

19. Figure S15. ¹ H-NMR spectra of 4-nitrophenyl benzoate (2p)	S17
20. Figure S16. ¹³ C-NMR spectra of 4-nitrophenyl benzoate (2p)	S17
21. Figure S17. ¹ H-NMR spectra of Naphthalen-2-yl benzoate (2s)	S18
22. Figure S18. ¹³ C-NMR spectra of Naphthalen-2-yl benzoate (2s)	S18
23. Figure S19. ¹ H-NMR spectra of Quinolin-8-yl benzoate (2t)	S19
24. Figure S20. ¹³ C-NMR spectra of Quinolin-8-yl benzoate (2t)	S19
25. Figure S21. ¹ H-NMR spectra of 2-oxo-1,2-diphenylethyl benzoate (2x)	S20
26. Figure S22. ¹³ C-NMR spectra of 2-oxo-1,2-diphenylethyl benzoate (2x)	S20
27. Figure S23. ¹ H-NMR spectra of Isopentyl 3,5-dinitrobenzoate (4b)	S21
28. Figure S24. ¹³ C-NMR spectra of Isopentyl 3,5-dinitrobenzoate (4b)	S21
29. Figure S25. ¹ H-NMR spectra of 2-chloroethyl 3,5-dinitrobenzoate (4c)	S22
30. Figure S26. ¹³ C-NMR spectra of 2-chloroethyl 3,5-dinitrobenzoate (4c)	S22
31. Figure S27. ¹ H-NMR spectra of Cyclohexyl 3,5-dinitrobenzoate (4e)	S23
32. Figure S28. ¹³ C-NMR spectra of Cyclohexyl 3,5-dinitrobenzoate (4e)	S23
33. Figure S29. ¹ H-NMR spectra of Benzyl 3,5-dinitrobenzoate (4f)	S24
34. Figure S30. ¹³ C-NMR spectra of Benzyl 3,5-dinitrobenzoate (4f)	S24
35. Figure S31. ¹ H-NMR spectra of Cinnamyl 3,5-dinitrobenzoate (4g)	S25
36. Figure S32. ¹³ C-NMR spectra of Cinnamyl 3,5-dinitrobenzoate (4g)	S25
37. Figure S33. ¹ H-NMR spectra of 2-formylphenyl 3,5-dinitrobenzoate (4i)	S26
38. Figure S34. ¹³ C-NMR spectra of 2-formylphenyl 3,5-dinitrobenzoate (4i)	S26

Address correspondence to Suchandra Chakraborty, Department of Clinical and Experimental Pharmacology, School of Tropical Medicine, 108, Chittaranjan Avenue, Kolkata – 700073, India. E-mail: suchandra82@ymail.com.

1. General procedure for benzoylation of phenols

Phenolic compound (20.0 mmol) was mixed with well grinded K_2CO_3 (1.5 g, 10.0 mmol) and NaCl (1.5 g) mixture (in case of solid phenols, it should be grinded along with the reaction mixture) and transferred into the quartz reaction vessel. To this reaction mixture benzoyl chloride (2.3 mL, 20.0 mmol) was added and mixed thoroughly. The reaction vessel was placed into the microwave reactor under sealed condition with a stirrer and irradiated at the power of 100 W, 70 °C and 5 bar (maximum pressure) for 2 mins. During reaction, the pressure of the reaction vessel raised to 4.8 bar. The completion of the reaction was monitored through TLC. After completion of the reaction the reactor was allowed to cool along with the reaction vessel for 10 mins. The reaction mixture was then poured into ice-water. The solid product thus obtained was filtered and washed with cold water. It was then recrystallised from methanol-water to obtain the desired benzoyl derivatives.

2. General procedure for 3,5-dinitrobenzoylation of alcohols/ phenols

3,5-dinitrobenzoyl chloride (10.0 mmol) was blended well with anhydrous K_2CO_3 (0.75 g, 5.0 mmol) and NaCl (0.75 g) in a mortar pestle. Then reaction mixture was taken in the microwave vessel and alcohol/ phenol (10.0 mmol) was added to it and mixed thoroughly. The reaction vessel was positioned into the microwave reactor under sealed condition with a stirrer and irradiated at a power of 100 W, 110°C and 5 bar (maximum pressure) for 2 mins. During reaction, the reactor read the maximum pressure as 3.2 bar. After completion, the reactor was allowed to run for 10 mins to purge the compressed air to cool the reaction vessel. The reaction mixture was then transferred into ice-water. The solid product was then collected through

filtration and washed with cold water. Then 3,5-dinitrobenzoate was purified by crystallization from methanol-water to furnish the product.

3. Characteristics Spectral data for the representative benzoates

2,3-dimethylphenyl benzoate (2d)^d. The compound was recrystallised from MeOH-water to yield white crystals, 93% yield, m.p. 54°C. UV λ_{max} : 235 nm. IR (KBr, ν_{max} cm^{-1}): 3427, 2948, 1724, 1685, 1600, 1581 cm^{-1} . ^1H NMR (CDCl_3 , 500 MHz) δ 2.15 (s, 3H), 2.34 (s, 3H), 7.00 (d, J 8.0 Hz, 1H), 7.10 (d, J 7.5 Hz, 1H), 7.17 (t, 1H), 7.54 (t, 2H), 7.66 (t, 1H), 8.25 (d, J 7.6 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.5, 20.1, 119.5, 126.1, 127.5, 128.62 ($\times 2$), 128.9, 129.6, 130.1($\times 2$), 133.5, 138.5, 149.4, 165.0. HRMS: m/z calcd. for $\text{C}_{15}\text{H}_{14}\text{O}_2$: 249.0887 ($\text{M} + \text{Na}$); found 249.0884.

2-isopropyl-5-methylphenyl benzoate (2f)^[35]. The compound was recrystallised from MeOH to obtain white crystals, 83% yield, m.p. 34°C. UV λ_{max} : 239 nm, IR (KBr, ν_{max} cm^{-1}): 3430, 2848, 1722, 1680, 1590, 1561 cm^{-1} . ^1H NMR (CDCl_3 , 500 MHz) δ 1.26 (t, 6H), 2.37 (s, 3H), 3.09 – 3.21 (m, 1H), 6.99 (s, 1H), 7.10 (d, J 7.5 Hz, 1H), 7.28 (d, J 8.0 Hz, 1H), 7.55 (t, 2H), 7.67 (t, 1H), 8.26 (d, J 8.5 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 20.9, 23.1, 26.8, 27.4, 116.1, 121.6, 123.0, 126.3, 127.3, 128.7, 130.2, 131.5, 133.6, 136.7, 148.3, 152.8, 165.5. HRMS: m/z calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_2$: 277.1199 ($\text{M} + \text{Na}$); found 277.1197.

4-chlorophenyl benzoate (2h)^[36]. The compound was recrystallised from MeOH-water to furnish white crystals, 86% yield, m.p. 91°C. UV λ_{max} : 242 nm. IR (KBr, ν_{max} cm^{-1}): 3448, 3062, 1733, 1689, 1600, 1585, 1489 cm^{-1} . ^1H NMR (CDCl_3 , 500 MHz) δ 7.16-7.19 (dd, J 3.0 Hz, J 3.5 Hz, 2H), 7.40 (t, 2H), 7.51 (t, 2H), 7.64 (t, 1H), 8.19 (d, J 8.0 Hz, 2H). ^{13}C NMR

(CDCl₃, 125 MHz) δ 123.2 ($\times 2$), 128.7 ($\times 2$), 129.3, 129.6($\times 2$), 130.3($\times 2$), 131.4, 133.9, 149.6, 165.0. HRMS: m/z calcd. for C₁₃H₉O₂Cl: 255.0185 (M + Na); found 255.0188.

1,4-phenylene dibenzoate (2k)^[37]. The compound was recrystallised from MeOH to obtain white crystals, 68% yield, m.p. 198°C. UV $\lambda_{\max}$: 254nm. IR (KBr, $\nu_{\max}$ cm⁻¹): 3438, 3071, 1731, 1686, 1598, 1582 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz) δ 7.29 (s, 4H), 7.53 (t, 4H), 7.65 (t, 2H), 8.22 (d, J 7.5 Hz, 4H). ¹³C NMR (CDCl₃, 125 MHz) δ 122.8 ($\times 4$), 128.7 ($\times 4$), 129.5($\times 2$), 130.3($\times 4$), 133.8 ($\times 2$), 148.5 ($\times 2$), 165.2 ($\times 2$). HRMS: m/z calcd. for C₂₀H₁₄O₄: 319.0966 (M+H); found 319.0968.

2-formylphenyl benzoate (2l)^[38]. Liq. White oil, 85% yield. UV $\lambda_{\max}$: 265 nm. IR (KBr, $\nu_{\max}$ cm⁻¹): 3339, 3010, 2843, 2734, 1733, 1698, 1688, 1589, 1547 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz) δ 6.97 - 7.02 (q, 1H), 7.25 (d, J 8 Hz, 1H), 7.34 (t, 1H), 7.41-7.55 (m, 1H), 7.62-7.69 (m, 2H), 7.94 – 7.96 (dd, J 1.5 Hz, J 1.5 Hz, 1H), 8.23 (d, J 8 Hz, 2H), 10.22 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 119.8, 120.7, 123.6, 126.5, 128.7, 130.2, 133.7, 135.3, 137.0, 152.3, 161.6, 165.0, 188.4, 196.6. HRMS: m/z calcd. for C₁₄H₁₀O₃: 227.0705 (M + H); found 227.0708.0.

4-formyl-2-methoxyphenyl benzoate (2n)^[39]. The compound was recrystallised from MeOH-water to obtain white crystals, 91% yield. UV $\lambda_{\max}$: 262 nm. IR (KBr, $\nu_{\max}$ cm⁻¹): 3343, 2989, 2829, 2736, 1736, 1702, 1688, 1600, 1540 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz) δ 3.89 (s, 3H), 7.35 (d, J 7.5 Hz, 1H), 7.51 – 7.55 (m, 4H), 7.65 (t, 1H), 8.21(d, J 7.5 Hz, 2H), 9.97 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 56.2, 111.1, 123.7, 124.8, 128.5, 128.6, 129.0, 130.4, 130.5, 133.9, 135.4, 145.4, 152.3, 164.2, 191.1. HRMS: m/z calcd. for C₁₅H₁₂O₄: 257.0810 (M + H); found 257.0811.

4-nitrophenyl benzoate (2p)^[40]. The compound was recrystallised from MeOH-water to obtain white crystals, 82% yield. UV $\lambda_{\max}$: 278 nm. IR (KBr, $\nu_{\max}$ cm⁻¹): 3528, 3114, 1735,

1697, 1614, 1591 cm^{-1} . ^1H NMR (CDCl_3 , 500 MHz) δ 7.41-7.44 (dd, J 3.0 Hz, J 3.0 Hz, 2H), 7.54 (t, 2H), 7.68 (t, 1H), 8.20 (d, J 8.5 Hz, 2H), 8.31-8.34 (dd, J 3.0 Hz, J 3.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 122.7 ($\times 2$), 125.4 ($\times 2$), 128.7, 128.9 ($\times 2$), 130.4($\times 2$), 134.3, 145.5, 155.9, 164.3. HRMS: m/z calcd. for $\text{C}_{13}\text{H}_9\text{NO}_4$: 266.0425 ($\text{M} + \text{Na}$); found 266.0428.

Naphthalen-2-yl benzoate (2s)^[41]. The compound was recrystallised from MeOH-water to obtain white crystals, 86% yield. UV λ_{max} : 280 nm. IR (KBr, ν_{max} cm^{-1}): 3446, 3056, 1730, 1625, 1596, 1581 cm^{-1} . ^1H NMR (CDCl_3 , 500 MHz) δ 7.36-7.39 (dd, J 2.5 Hz, J 3.0 Hz, 1H), 7.47 – 7.56 (m, 4H), 7.65 – 7.71 (m, 2H), 7.83 -7.93 (m, 3H), 8.27 (d, J 9.5 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 118.8, 121.3, 125.8, 126.7, 127.8, 128.6, 128.8, 129.6 ($\times 2$), 129.7, 130.3 ($\times 2$), 131.6, 133.7, 133.9, 148.7, 165.5. HRMS: m/z calcd. for $\text{C}_{17}\text{H}_{12}\text{O}_2$: 271.0731 ($\text{M} + \text{Na}$); found 271.0729.

Quinolin-8-yl benzoate (2t)^[42]. The compound was recrystallised from MeOH-water to obtain white crystals, 88% yield. UV λ_{max} : 298 nm. IR (KBr, ν_{max} cm^{-1}): 3442, 3060, 1731, 1691, 1595, 1579 cm^{-1} . ^1H NMR (CDCl_3 , 500 MHz) δ 7.41-7.46 (m, 1H), 7.52 – 7.61 (m, 4H), 7.66 (t, 1H), 7.75 -7.78 (m, 1H), 8.17 - 8.21 (m, 1H), 8.36 (d, J 9.0 Hz, 2H), 8.90 – 8.91(dd, J 2.0 Hz, J 2.0 Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 110.5, 118.0, 121.8, 126.2, 128.0, 128.7, 129.7, 130.7, 133.6, 136.1, 136.7, 141.5, 147.6, 147.8, 150.7, 165.6. HRMS: m/z calcd. for $\text{C}_{16}\text{H}_{11}\text{NO}_2$: 250.0864 ($\text{M} + \text{H}$); found 250.0862.

2-oxo-1,2-diphenylethyl benzoate (2x)^[43]. The compound was recrystallised from MeOH-water to obtain white crystals, 88% yield. UV λ_{max} : 264 nm. IR (KBr, ν_{max} cm^{-1}): 3433, 3017, 1736, 1698, 1592, 1574 cm^{-1} . ^1H NMR (CDCl_3 , 500 MHz) δ 5.95 (s, 1H), 7.29-7.35 (m, 3H), 7.37- 7.43 (m, 3H), 7.45-7.47 (m, 2H), 7.49-7.53 (m, 1H), 7.91 (d, J 7.5 Hz, 1H), 7.98-8.01 (m, 3H), 8.10 (d, J 8.5 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 78.0, 127.9, 128.5, 128.7, 128.9,

129.1, 129.2, 129.4, 129.5, 129.9, 130.0, 133.1, 133.4, 133.5, 133.7, 133.9, 134.9, 135.9, 139.1, 166.1, 193.8. HRMS: m/z calcd. for $C_{21}H_{16}O_3$: 317.1193 ($M + H$); found 317.1175.

Isopentyl 3,5-dinitrobenzoate (4b)^d. The compound was recrystallised from MeOH to obtain white crystals, 88% yield. UV λ_{max} : 238 nm. IR (KBr, ν_{max} cm^{-1}): 3440, 3101, 2963, 1722, 1629, 1542 cm^{-1} . 1H NMR ($CDCl_3$, 500 MHz) δ 1.01 (d, J 6.5 Hz, 6H), 1.72 – 1.81 (m, 3H), 4.49 (t, 2H), 9.13 (s, 2H), 9.20 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.5 ($\times 2$), 25.3, 26.2, 65.8, 122.4 ($\times 2$), 129.5 ($\times 2$), 134.3, 148.8, 162.7. HRMS: m/z calcd. for $C_{12}H_{14}N_2O_6$: 305.0743 ($M + Na$); found 305.0740.

2-chloroethyl 3,5-dinitrobenzoate (4c)^[44]. The compound was recrystallised from MeOH to obtain white crystals, 76% yield. UV λ_{max} : 235 nm. IR (KBr, ν_{max} cm^{-1}): 3464, 3089, 2964, 2880, 1732, 1652, 1629, 1545 cm^{-1} . 1H NMR ($CDCl_3$, 500 MHz) δ 3.88 (t, 2H), 4.72 (t, 2H), 9.18 (d, J 9 Hz, 2H), 9.24 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 41.3, 66.2, 122.8, 129.7, 133.2, 133.4, 148.9 ($\times 2$), 162.3. HRMS: m/z calcd. for $C_9H_7N_2O_6Cl$: 275.0066 ($M + H$); found 275.0068.

Benzyl 3,5-dinitrobenzoate (4f)^[45]. The compound was recrystallised from MeOH to obtain white crystals, 88% yield. UV λ_{max} : 227 nm. IR (KBr, ν_{max} cm^{-1}): 3422, 3100, 1719, 1630, 1547 cm^{-1} . 1H NMR ($CDCl_3$, 500 MHz) δ 5.48 (s, 2H), 7.38 – 7.44 (m, 3H), 7.48 (d, J 6.5 Hz, 2H), 9.16 (s, 2H), 9.20 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 68.7, 122.5, 128.9 ($\times 2$), 129.0 ($\times 2$), 129.1, 129.6 ($\times 2$), 134.0, 134.6, 148.8 ($\times 2$), 162.5. HRMS: m/z calcd. for $C_{14}H_{10}N_2O_6$: 325.0431 ($M + Na$); found 325.0430.

Cinnamyl 3,5-dinitrobenzoate (4g)^d. The compound was recrystallised from MeOH to obtain white crystals, 74% yield. UV λ_{max} : 287 nm. IR (KBr, ν_{max} cm^{-1}): 3462, 3107, 3089, 1733, 1683, 1629, 1548, 1541 cm^{-1} , 1H NMR ($CDCl_3$, 500 MHz) δ 5.11 (d, J 6.5 Hz, 2H), 6.39-

6.44 (m, 1H), 6.80 (d, J 16.0 Hz, 1H), 7.26-7.30 (m, 1H), 7.35 (t, 2H), 7.43 (d, J 7.0 Hz, 2H), 9.19-9.22 (dd, J 2.0 Hz, J 2.0 Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 67.6, 121.6, 122.5, 126.9 ($\times 2$), 128.7 ($\times 2$), 128.8 ($\times 2$), 129.6 ($\times 2$), 134.0, 135.7, 136.5, 148.8, 162.4. HRMS: m/z calcd. for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_6$: 329.0768 ($M + H$); found 329.0764.

2-formylphenyl 3,5-dinitrobenzoate (4i)^d. The compound was recrystallised from MeOH to obtain white crystals, 72% yield. UV λ_{max} : 274 nm. IR (KBr, ν_{max} cm^{-1}): 3340, 3016, 2844, 2737, 1735, 1692, 1678, 1581, 1545 cm^{-1} . ^1H NMR (CDCl_3 , 500 MHz) δ 7.34 (d, J 10.0 Hz, 1H), 7.58 (t, 1H), 7.76 (q, 1H), 7.94 (d, J 7.5 Hz, 1H), 9.30 – 9.33 (m, 3H), 10.01 (s, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 123.0, 123.5, 127.6, 127.7, 129.9 ($\times 2$), 130.1, 133.1, 134.4, 135.7, 148.9, 149.5, 161.3, 189.3. HRMS: m/z calcd. for $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_7$: ($M + H$); found 317.0405.

4. REFERENCES

35. Ateeque, A.; Aggarwal, K. K.; Kumar, S. Carbon-13 and proton NMR shift assignments of some thymol derivatives. *Indian Perfumer* **2002**, 46(2), 145.
36. (a) Lee, C. K.; Yu, J. S.; Lee, H. Determination of aromaticity indices of thiophene and furan by nuclear magnetic resonance spectroscopic analysis of their phenyl esters. *J. Het. Chem.* 2002, 39(6), 1207. (b) Vilve, N.; Oksana, T.; Signe, V.; Ivo, L.; Mare, P.; Vahur, M.; Ivar, K.; Ilmar A, K. Influence of substituents on the infrared stretching frequencies of carbonyl group in esters of benzoic acid. *J. Phys. Org. Chem.* 2006, 19(10), 654.
37. Wei, R. Molybdenum hexacarbonyl mediated alkoxycarbonylation of aryl halides. *Synthesis* **2011**, 14, 2303.
38. Luis E, E. Preparation of 6-benzyloxy-spirobenzopyran-indoline compounds and the evaluation of their optical activities. *Dyes and Pigments* **2008**, 78(2), 111.

39. (a) Na, Q. A green chemistry method for the regeneration of carbonyl compounds from oximes by using cupric chloride dihydrate as a recoverable promoter for hydrolysis. *Synlett* **2011**, 7, 1028. (b) Dikumar, E. A. Esters Derived from Vanillin and Vanillal and Aromatic and Functionalized Aliphatic Carboxylic Acids. *Russian J. Org. Chem.* **2005**, 41(7), 992.
40. Lee, C. K. Determination of aromaticity indices of thiophene and furan by nuclear magnetic resonance spectroscopic analysis of their phenyl esters. *J. Het. Chem.* **2002**, 39(6), 1207.
41. (a) Rosa, J. N. NHC-Iron-Catalyzed Aerobic Oxidative Aromatic Esterification of Aldehydes using Boronic Acids. *Org. Lett.* **2010**, 12(12), 2686. (b) Chen, C. Nucleophilic acyl substitutions of anhydrides with protic nucleophiles catalyzed by amphoteric, oxomolybdenum species. *J. Org. Chem.* **2005**, 70(4), 1188.
42. Zhang, H. 8-Hydroxyquinoline Benzoates as Highly Sensitive Fluorescent Chemosensors for Transition Metal Ions. *Org. Lett.* **2005**, 7(19), 4217.
43. Cutulic, S. P. Y. Metal-Free Reductive Cleavage of C-O σ -bonds in Acylol Derivatives by an Organic Neutral Super-Electron-Donor. *J. Org. Chem.* **2009**, 74(22), 8713.
44. Lown, J. William, Synthesis of 3-(2-haloethyl)aryltriazenes and study of their reactions in aqueous solution, *Canadian J. Chem.* **1981**, 59(9), 1347.
45. But, T. Y. S. Organocatalytic Mitsunobu reactions with 3,5-dinitrobenzoic acid. *Synlett* **2010**, 7, 1115.

5. **Figure S3.** Method Set up for the benzylation of phenol in microwave reactor

6. **Figure S4.** Graph of the progress of the reaction

7. Figure S3. ^1H -NMR spectra of 2,3-dimethylphenyl benzoate (2d)

8. Figure S4. ^{13}C -NMR spectra of 2,3-dimethylphenyl benzoate (2d)

9. Figure S5. ¹H-NMR spectra of 2-isopropyl-5-methylphenyl benzoate (2f)

DSA.STM.S110-1H(SKD) 23dec14.23

10. Figure S6. ¹³C-NMR spectra of 2-isopropyl-5-methylphenyl benzoate (2f)

DSA.STM.S.110-13C(SKD) 24dec14.37

11. Figure S7. ^1H -NMR spectra of 4-chlorophenyl benzoate (2h)

12. Figure S8. ^{13}C -NMR spectra of 4-chlorophenyl benzoate (2h)

13. Figure S9. ¹H-NMR spectra of 1,4-phenylene dibenzoate (2k)

15. Figure S11. ¹H-NMR spectra of 2-formylphenyl benzoate (2I)

16. Figure S12. ¹³C-NMR spectra of 2-formylphenyl benzoate (2I)

17. Figure S13. ^1H -NMR spectra of 4-formyl-2-methoxyphenyl benzoate (2n)

18. Figure S14. ^{13}C -NMR spectra of 4-formyl-2-methoxyphenyl benzoate (2n)

19. Figure S15. ¹H-NMR spectra of 4-nitrophenyl benzoate (2p)

DSA.STM.S.101-1H (SKD) 23dec14.22

20. Figure S16. ¹³C-NMR spectra of 4-nitrophenyl benzoate (2p)

DSA.STM.S101-13C (SKD) 24dec14.40

21. Figure S17. ^1H -NMR spectra of Naphthalen-2-yl benzoate (2s)

22. Figure S18. ^{13}C -NMR spectra of Naphthalen-2-yl benzoate (2s)

23. Figure S19. ¹H-NMR spectra of Quinolin-8-yl benzoate (2t)

24. Figure S20. ¹³C-NMR spectra of Quinolin-8-yl benzoate (2t)

25. Figure S21. ¹H-NMR spectra of 2-oxo-1,2-diphenylethyl benzoate (2x)

26. Figure S22. ¹³C-NMR spectra of 2-oxo-1,2-diphenylethyl benzoate (2x)

27. Figure S23. ¹H-NMR spectra of Isopentyl 3,5-dinitrobenzoate (4b)

28. Figure S24. ¹³C-NMR spectra of Isopentyl 3,5-dinitrobenzoate (4b)

29. Figure S25. ¹H-NMR spectra of 2-chloroethyl 3,5-dinitrobenzoate (4c)

MDY2.108CS-1H (SKD) 23dec14.25

30. Figure S26. ¹³C-NMR spectra of 2-chloroethyl 3,5-dinitrobenzoate (4c)

MDY2.108CS-13C (SKD) 24dec14.41

33. Figure S29. ¹H-NMR spectra of Benzyl 3,5-dinitrobenzoate (4f)

34. Figure S30. ¹³C-NMR spectra of Benzyl 3,5-dinitrobenzoate (4f)

35. Figure S31. ¹H-NMR spectra of Cinnamyl 3,5-dinitrobenzoate (4g)

TD.S.107-1H(SKD) 10feb15.5

36. Figure S32. ¹³C-NMR spectra of Cinnamyl 3,5-dinitrobenzoate (4g)

TD.S.107-13C(SKD) 11mar15.12

37. Figure S33. ^1H -NMR spectra of 2-formylphenyl 3,5-dinitrobenzoate (4i)

38. Figure S34. ^{13}C -NMR spectra of 2-formylphenyl 3,5-dinitrobenzoate (4i)

ABP.C.S.112-13C (SKD)