Electronic Supplementary Material (ESI) for RSC Advances

Asymmetric transfer hydrogenation of unsymmetrical benzils

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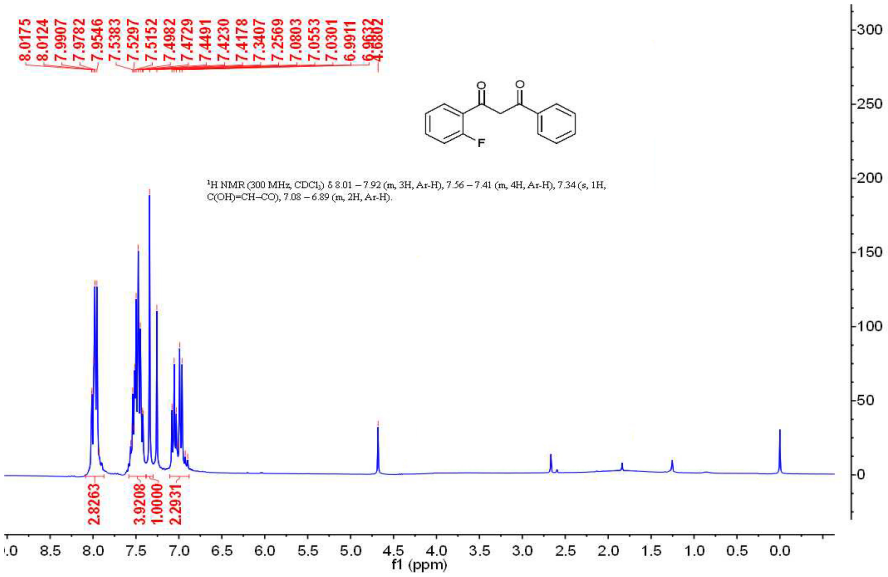
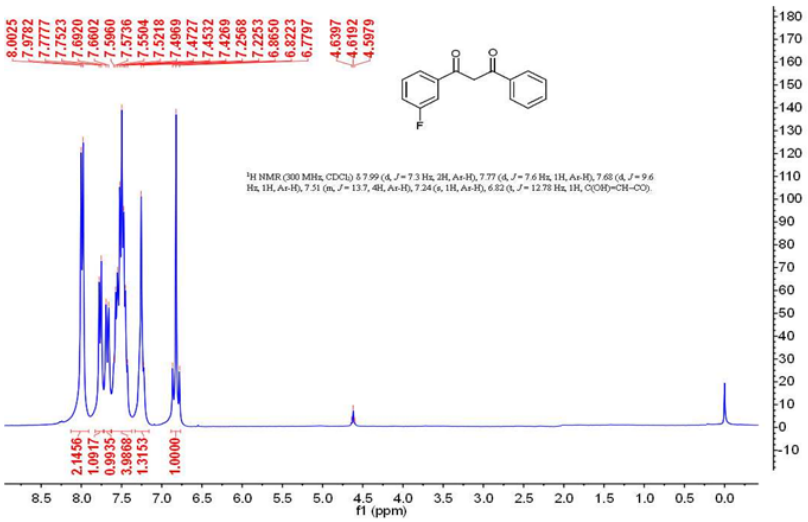
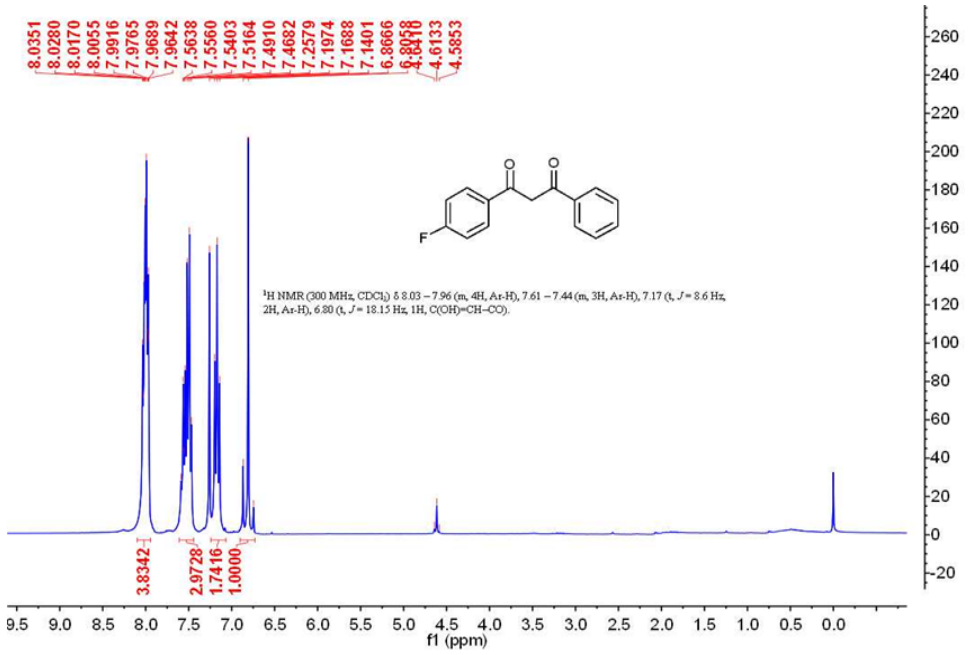
1. ^{1}H NMR spectra of 2a-f



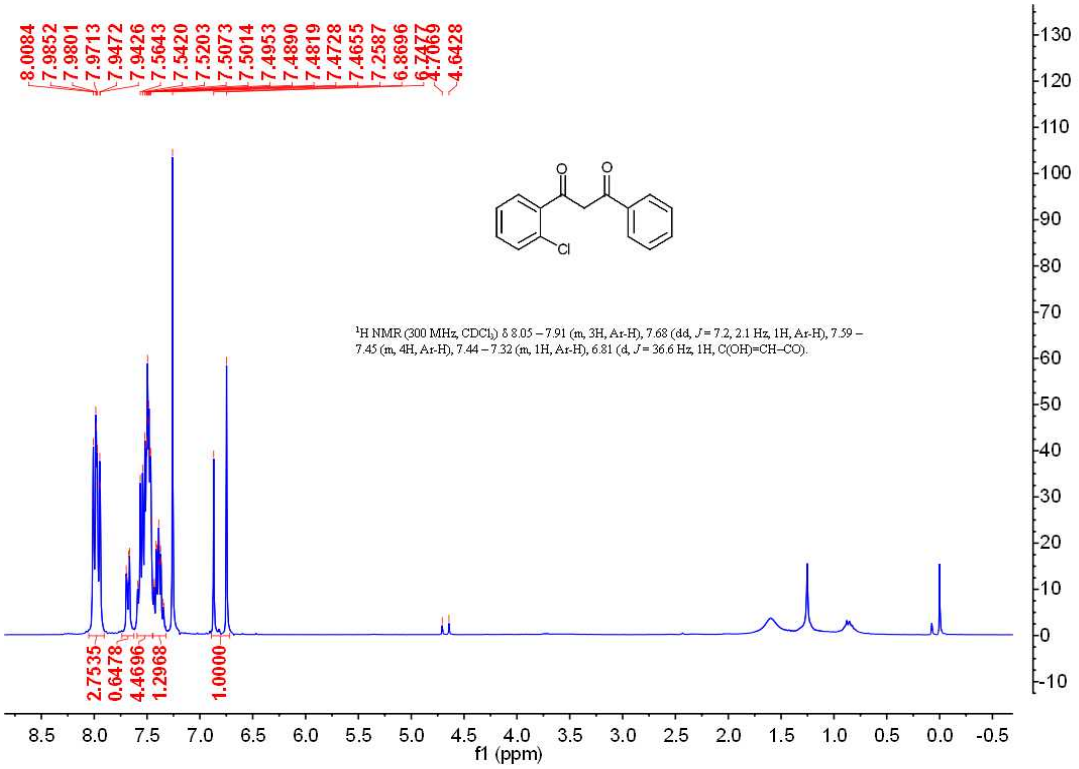
2a$_1$: 82 %, yellow solid,m.p. 59.8–61.2 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.01–7.92 (m, 3 H, Ar–H), 7.56–7.41 (m, 4 H, Ar–H), 7.34 (s, 1 H, C(OH)=CH–CO), 7.08–6.89 (m, 2 H, Ar–H). Anal. Calcd for $C_{15}H_{11}FO_2$: C, 74.37; H, 4.58; O, 13.21. Found: C, 74.32; H,4.63; O, 13.08. Mass (MS): m/z 242.9 $[M+H]^+$.



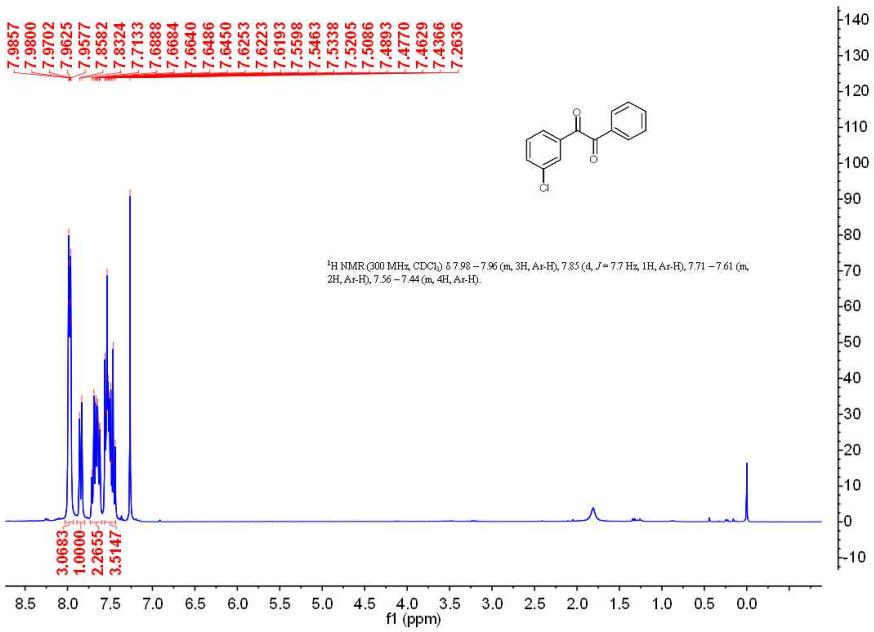
2a$_2$: 92 %, dark yellow solid, m.p. 85.5–86.4 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.99 (d, *J* = 7.3 Hz, 2 H, Ar–H), 7.77 (d, *J* = 7.6 Hz, 1 H, Ar–H), 7.68 (d, *J* = 9.6 Hz, 1 H, Ar–H), 7.51 (m, *J* = 13.7, 4 H, Ar–H), 7.24 (s, 1 H, Ar–H), 6.82 (t, *J* = 12.78 Hz, 1 H, C(OH)=CH–CO). Anal. Calcd for $C_{15}H_{11}FO_2$: C, 74.37; H, 4.58; O, 13.21. Found: C, 74.29; H,4.62; O, 13.12. Mass (MS): m/z 243.0 $[M+H]^+$.



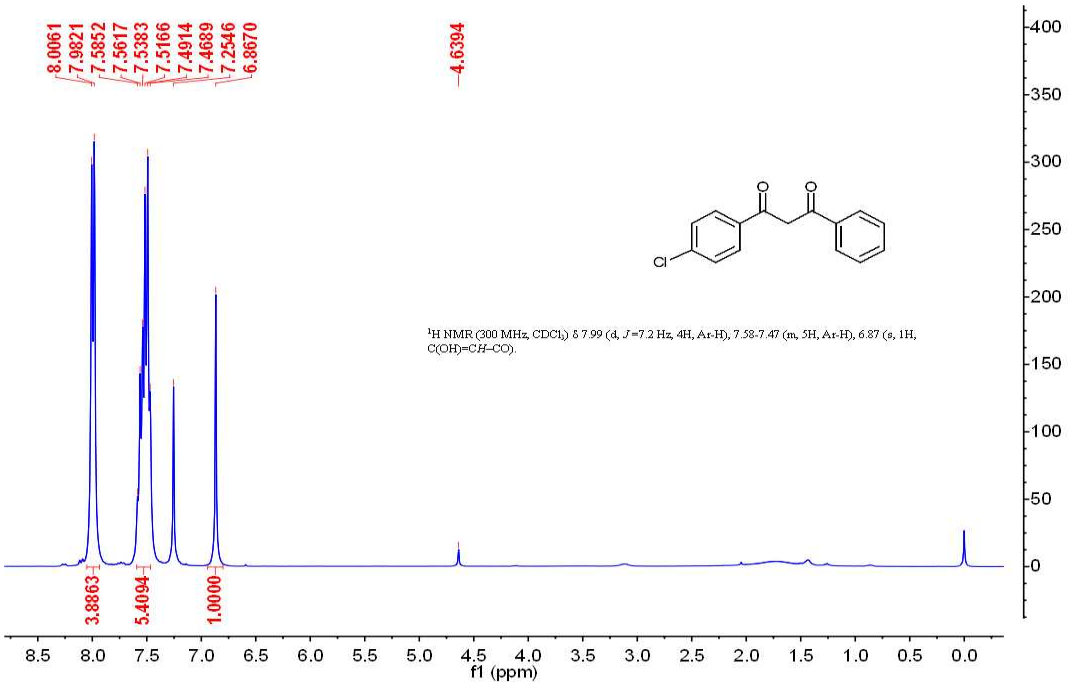
2a$_3$: 92 %, white solid, m.p. 118.7–120.7 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.03–7.96 (m, 4 H, Ar–H), 7.61–7.44 (m, 3 H, Ar–H), 7.17 (t, *J* = 8.6 Hz, 2 H, Ar–H), 6.80 (t, *J* = 18.15 Hz, 1 H, C(OH)=CH–CO). Anal. Calcd for $C_{15}H_{11}FO_2$: C, 74.37; H, 4.58; O, 13.21. Found: C, 74.35; H,4.63; O, 13.16. Mass (MS): m/z 243.1 $[M+H]^+$.



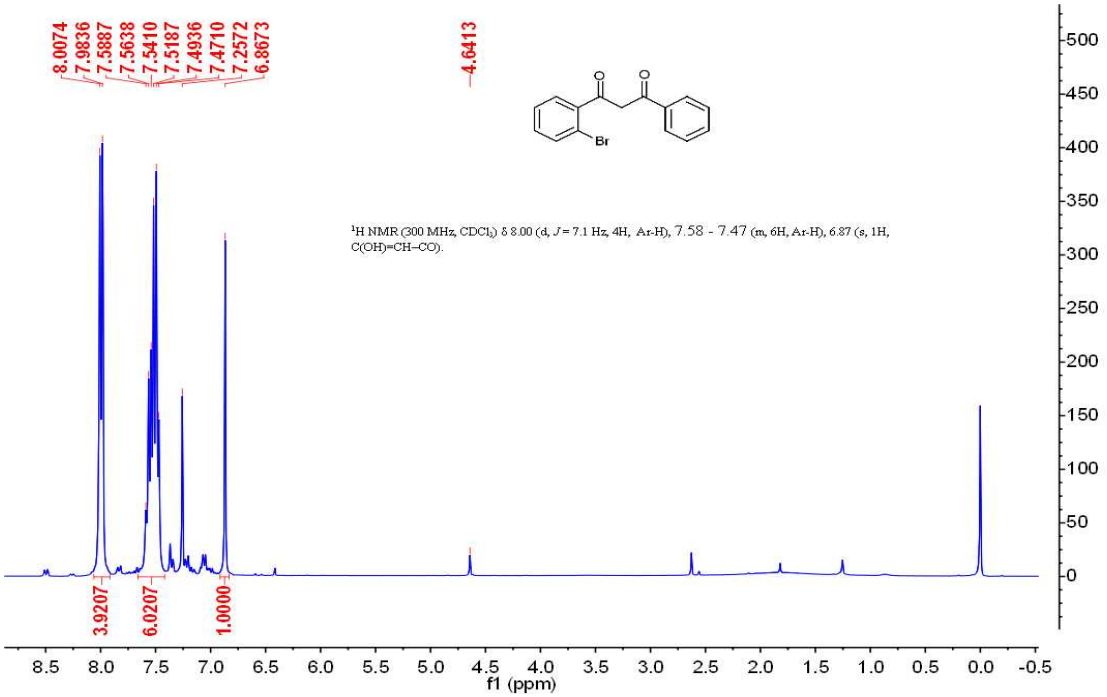
2b$_1$: 88 %, red-brown solid, m.p. 57.2–58.4 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.05–7.91 (m, 3 H, Ar–H), 7.68 (dd, *J* = 7.2, 2.1 Hz, 1 H, Ar–H), 7.59–7.45 (m, 4 H, Ar–H), 7.44–7.32 (m, 1 H, Ar–H), 6.81 (d, *J* = 36.6 Hz, 1 H, C(OH)=CH–CO). Anal. Calcd for $C_{15}H_{11}ClO_2$: C, 69.64; H, 4.27; O, 12.37. Found: C, 69.53; H,4.23; O, 12.29. Mass (MS): m/z 259.1 $[M+H]^+$.



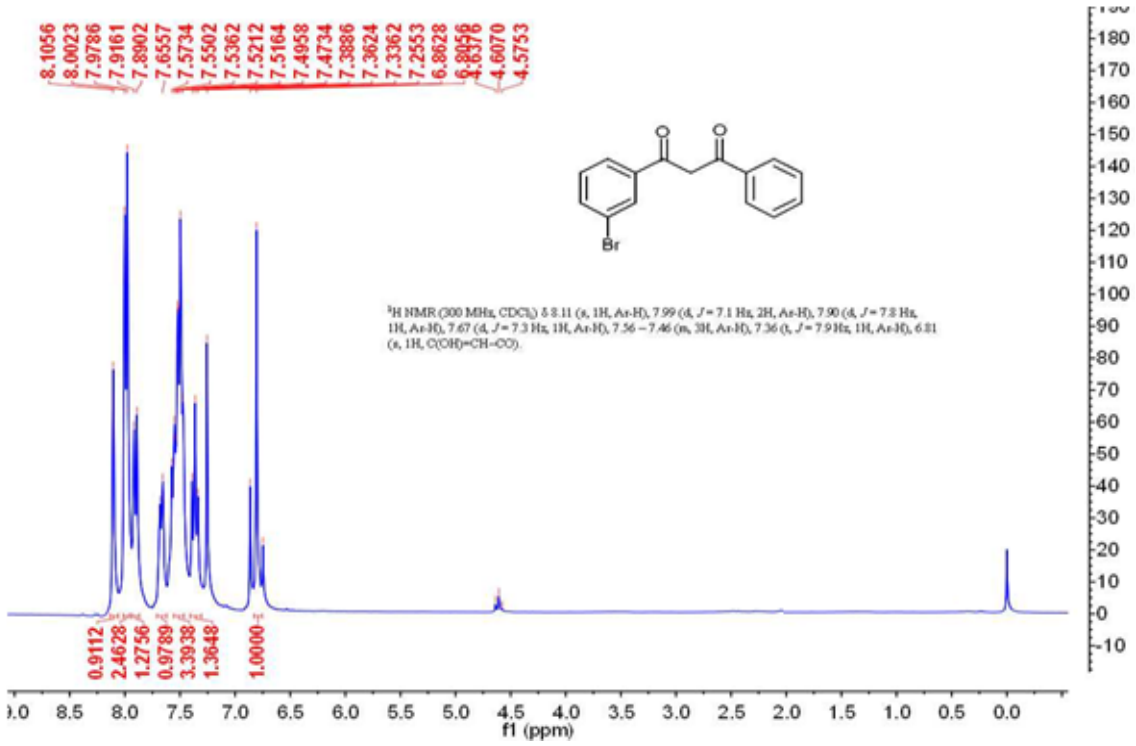
2b$_2$: 90% yield, brick-red solid,m.p. 69.3-70.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 3 H, Ar-H), 7.86 (d, J = 7.7 Hz, 1 H, Ar-H), 7.63 – 7.35 (m, 5 H, Ar-H), 6.90 – 6.71 (m, 1 H, C(OH)=CH–CO). Anal. Calcd for $C_{15}H_{11}ClO_2$: C, 69.64; H, 4.27; O, 12.37. Found: C, 69.61; H, 4.30; O, 12.35. Mass (MS): m/z 259.0 $[M+H]^+$.



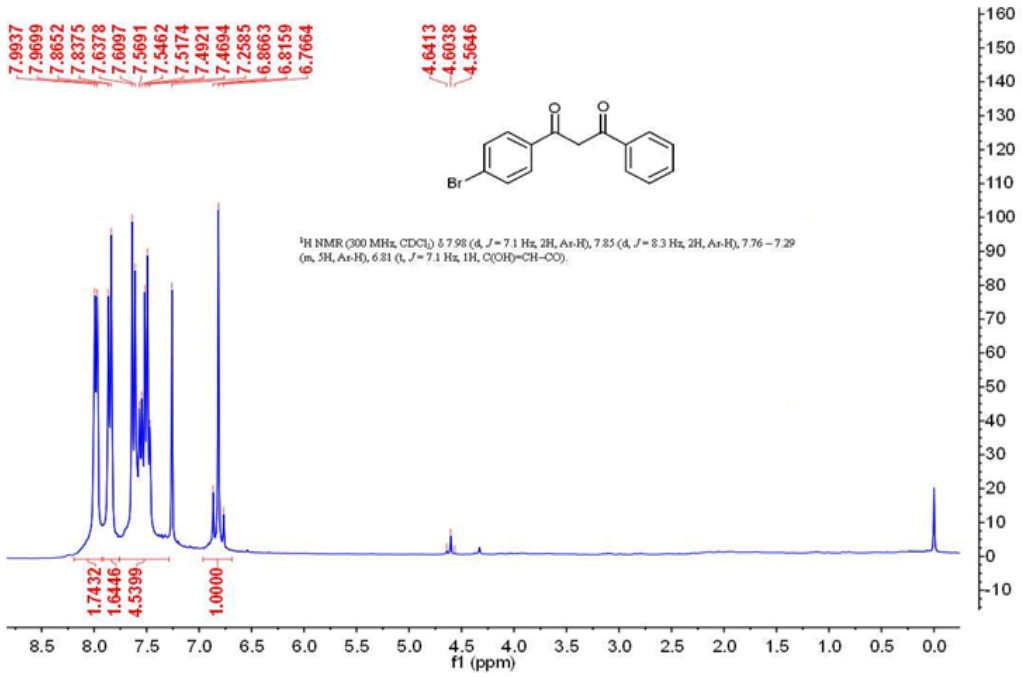
2b$_3$: 84 %, yellow solid, m.p. 86.9–87.6 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.99 (d, *J* = 7.2 Hz, 4 H, Ar–H), 7.58–7.47 (m, 5 H, Ar–H), 6.87 (s, 1 H, C(OH)=CH–CO). Anal. Calcd for $C_{15}H_{11}ClO_2$: C, 69.64; H, 4.27; O, 12.37. Found: C, 69.57; H, 4.32; O, 12.38. Mass (MS): m/z 259.0 $[M+H]^+$.



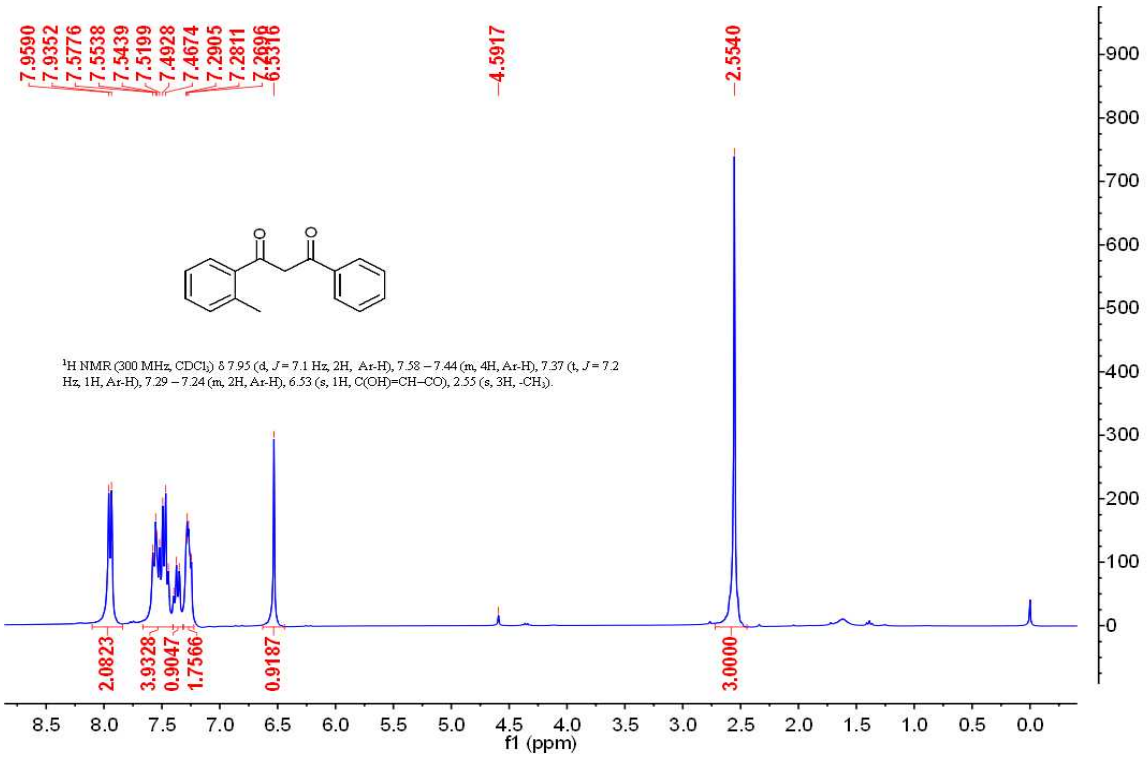
2c$_1$: 40 %, yellow solid, m.p 63–64 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.00 (d, *J* = 7.1 Hz, 3 H, Ar–H), 7.58–7.47 (m, 6 H, Ar–H), 6.87 (s, 1 H, C(OH)=CH–CO). Anal. Calcd for $C_{15}H_{11}BrO_2$: C, 59.43; H, 3.66; O, 10.56. Found: C, 59.38; H, 3.58; O, 10.47. Mass (MS): m/z 302.9 $[M+H]^+$.



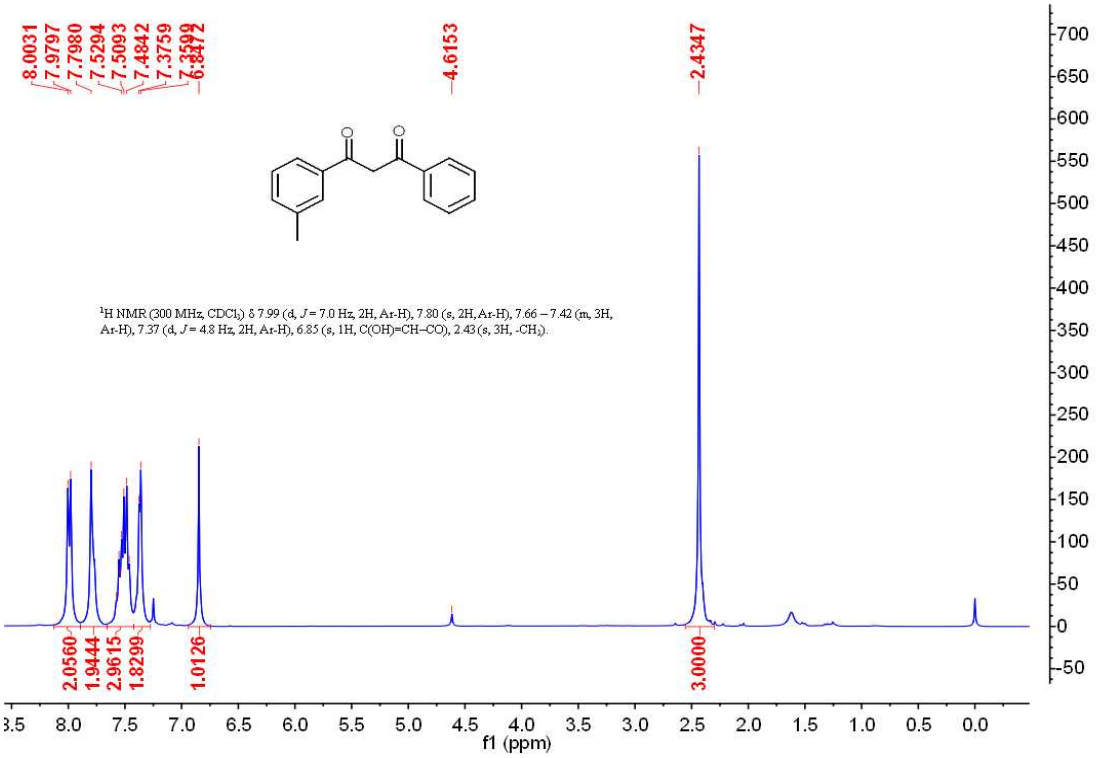
2c$_2$: 80 %, pink solid, m.p 63–64 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.11 (s, 1 H, Ar–H), 7.99 (d, *J* = 7.1 Hz, 2 H, Ar–H), 7.90 (d, *J* = 7.8 Hz, 1 H, Ar–H), 7.67 (d, *J* = 7.3 Hz, 1 H, Ar–H), 7.56 –7.46 (m, 3 H, Ar–H), 7.36 (t, *J* = 7.9 Hz, 1 H, Ar–H), 6.81 (s, 1 H, C(OH)=CH–CO). Anal. Calcd for $C_{15}H_{11}BrO_2$: C, 59.43; H, 3.66; O, 10.56. Found: C, 59.32; H, 3.60; O, 10.41. Mass (MS): m/z 303.0 $[M+H]^+$.



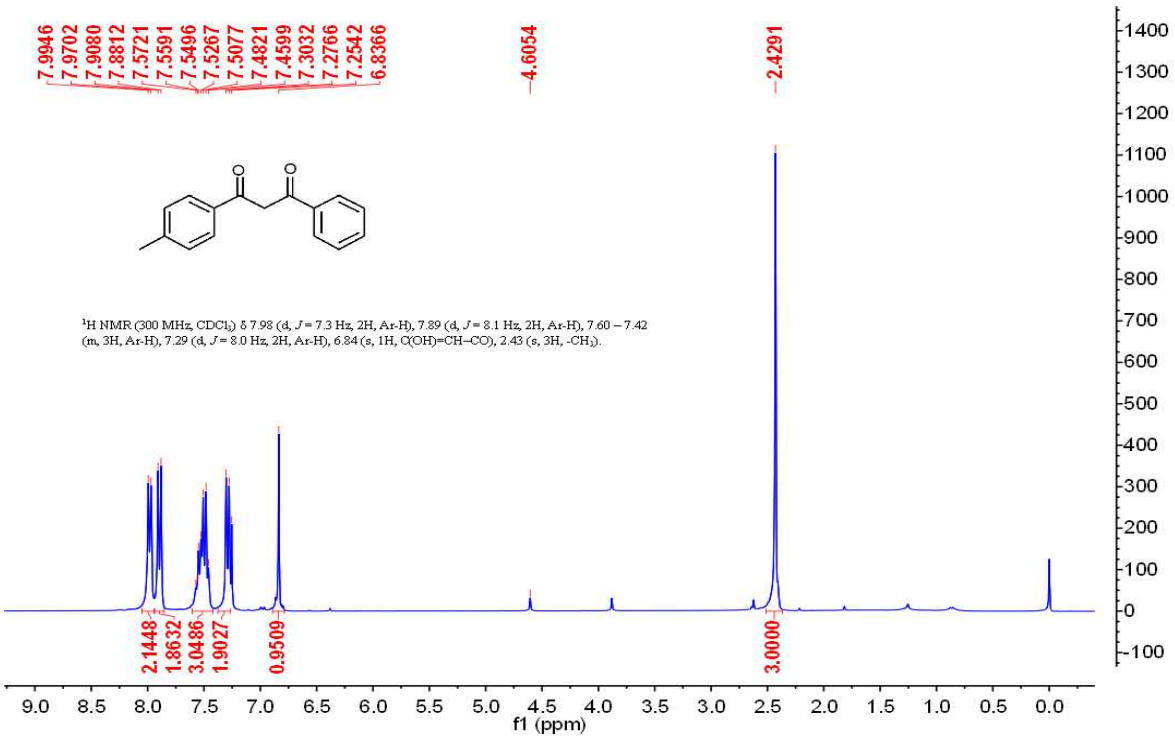
2c$_3$: 86 %, dark yellow solid, m.p. 93.1–93.8 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.98 (d, *J*=7.1 Hz, 2 H, Ar–H), 7.85 (d, *J*=8.3 Hz, 2 H, Ar–H), 7.76–7.29 (m, 5 H, Ar–H), 6.81 (t, *J* = 7.1 Hz, 1 H, C(OH)=CH–CO). Anal. Calcd for $C_{15}H_{11}BrO_2$: C, 59.43; H, 3.66; O, 10.56. Found: C, 59.32; H, 3.60; O, 10.41. Mass (MS): m/z 302.9 $[M+H]^+$.



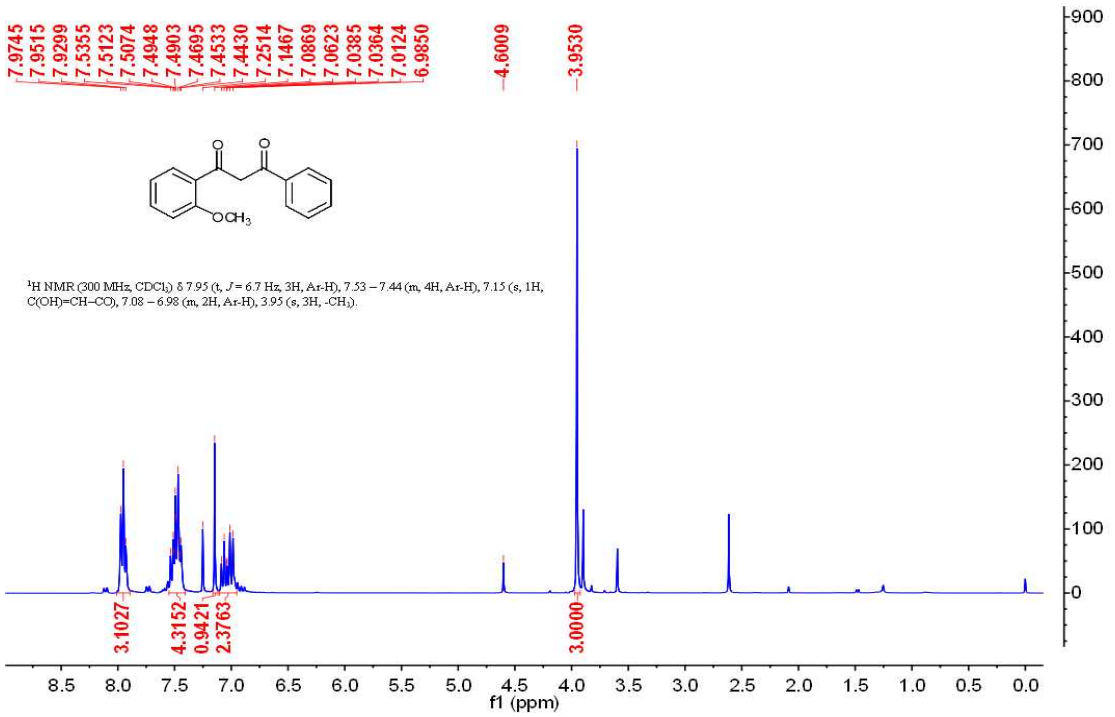
2d$_1$: 70 %, pink oil. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.95 (d, *J* = 7.1 Hz, 2 H, Ar–H), 7.58–7.44 (m, 4 H, Ar–H), 7.37 (t, *J* = 7.2 Hz, 1 H, Ar–H), 7.29–7.24 (m, 2 H, Ar–H), 6.53 (s, 1 H, C(OH)=CH–CO), 2.55 (s, 3 H, CH_3). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92; O, 13.43. Found: C, 80.49; H, 5.86; O, 13.38. Mass (MS): m/z 239.1 $[M+H]^+$.



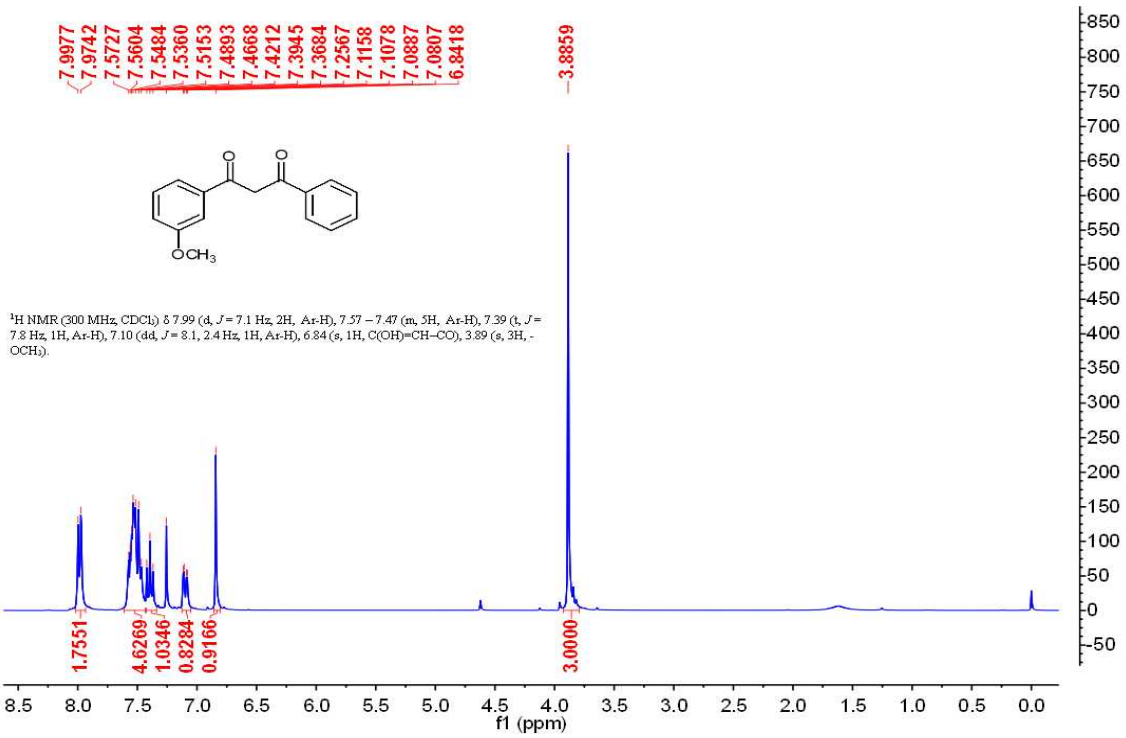
2d$_2$: 83 %, brick-red oil. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.99 (d, J = 7.0 Hz, 2 H, Ar–H), 7.80 (s, 2 H, Ar–H), 7.66–7.42 (m, 3 H, Ar–H), 7.37 (d, J = 4.8 Hz, 2 H, Ar–H), 6.85 (s, 1 H, C(OH)=CH–CO), 2.43 (s, 3 H, CH_3). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92; O, 13.43. Found: C, 80.58; H, 5.90; O, 13.34. Mass (MS): m/z 239.1 $[M+H]^+$.



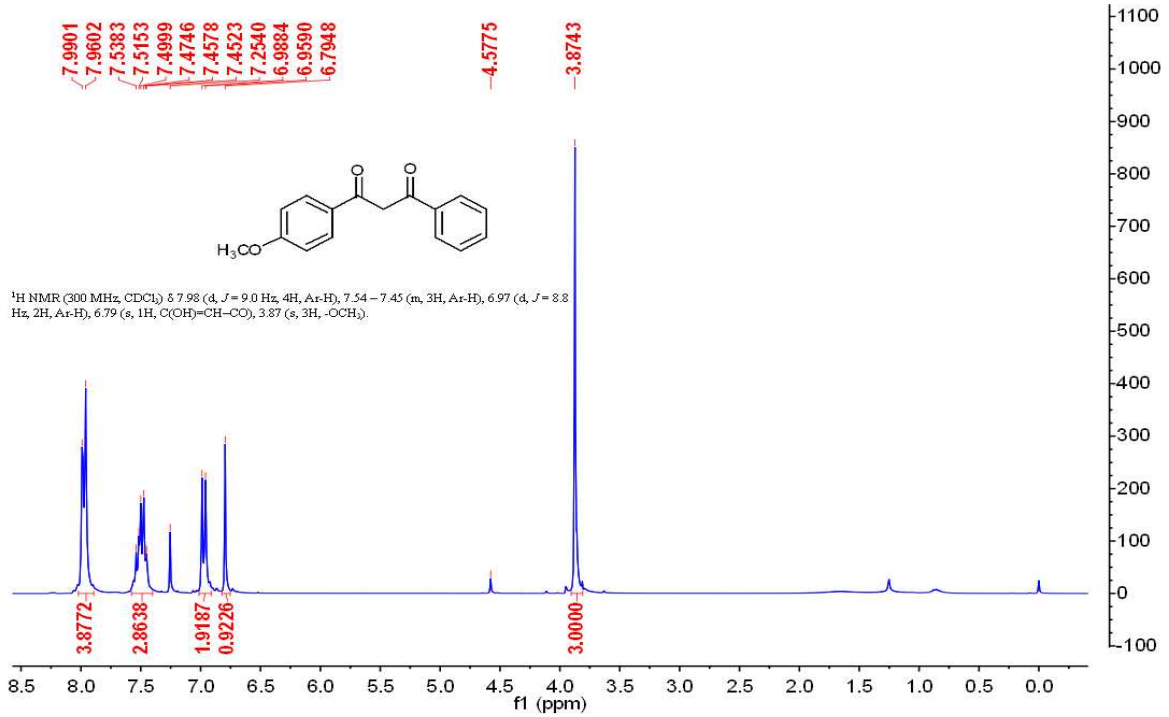
2d$_3$: 94 %, red-brown solid, m.p. 80–81.5 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.98 (d, J = 7.3 Hz, 2 H, Ar–H), 7.89 (d, J = 8.1 Hz, 2 H, Ar–H), 7.60-7.42 (m, 3 H, Ar–H), 7.29 (d, J = 8.0 Hz, 2 H, Ar–H), 6.84 (s, 1 H, C(OH)=CH–CO), 2.43 (s, 3 H, CH_3). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92; O, 13.43. Found: C, 80.59; H, 5.86; O, 13.44. Mass (MS): m/z 239.1 $[M+H]^+$.



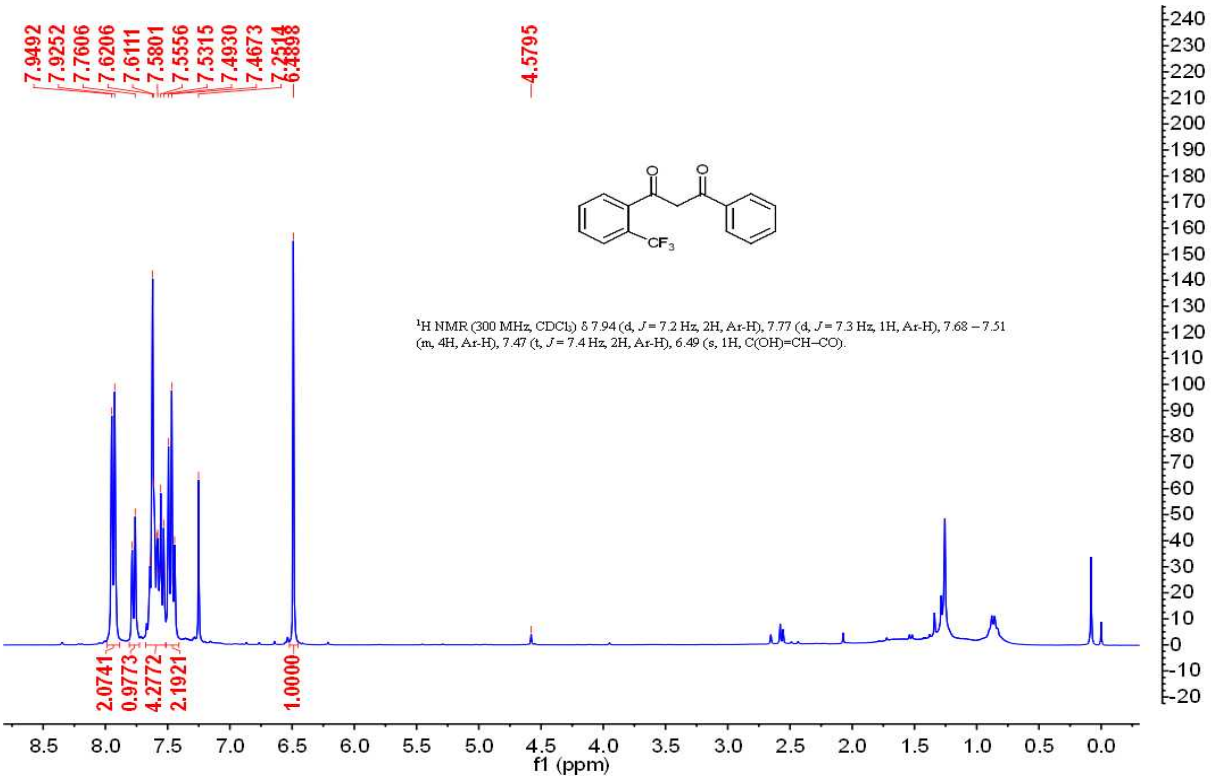
2e$_1$: 84 %, red-brown oil. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.95 (t, *J* = 6.7 Hz, 3 H, Ar–H), 7.53–7.44 (m, 4 H, Ar–H), 7.15 (s, 1 H, C(OH)=CH–CO), 7.08–6.98 (m, 2 H, Ar–H), 3.95 (s, 3 H, OCH_3). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55; O, 18.88. Found: C, 75.51; H, 5.46; O, 18.84. Mass (MS): m/z 255.1 $[M+H]^+$.



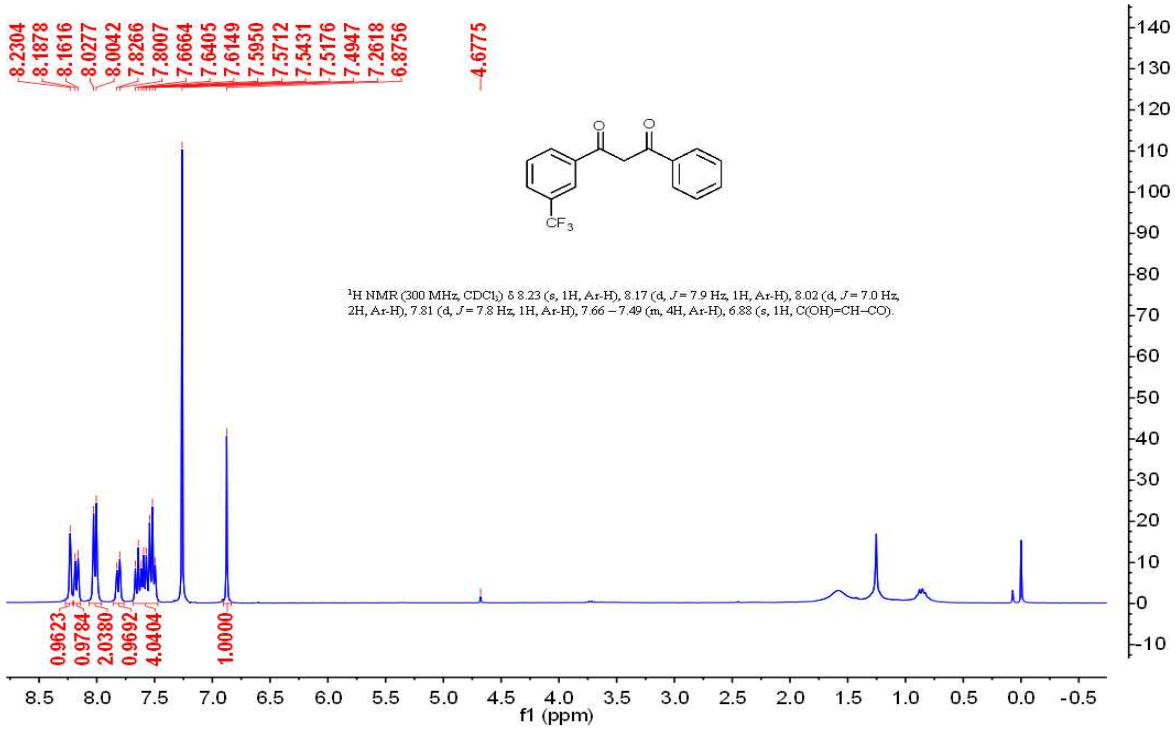
2e$_2$: 88 %, yellow-brown solid, m.p. 59–60 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.99 (d, *J* = 7.1 Hz, 2 H, Ar–H), 7.57-7.47 (m, 5 H, Ar–H), 7.39 (t, *J*=7.8 Hz, 1 H, Ar–H), 7.10 (dd, *J*=8.1, 2.4 Hz, 1 H, Ar–H), 6.84 (s, 1 H, C(OH)=CH–CO), 3.89 (s, 3 H, OCH_3). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55; O, 18.88. Found: C, 75.56; H, 5.51; O, 18.79. Mass (MS): m/z 255.0 $[M+H]^+$.



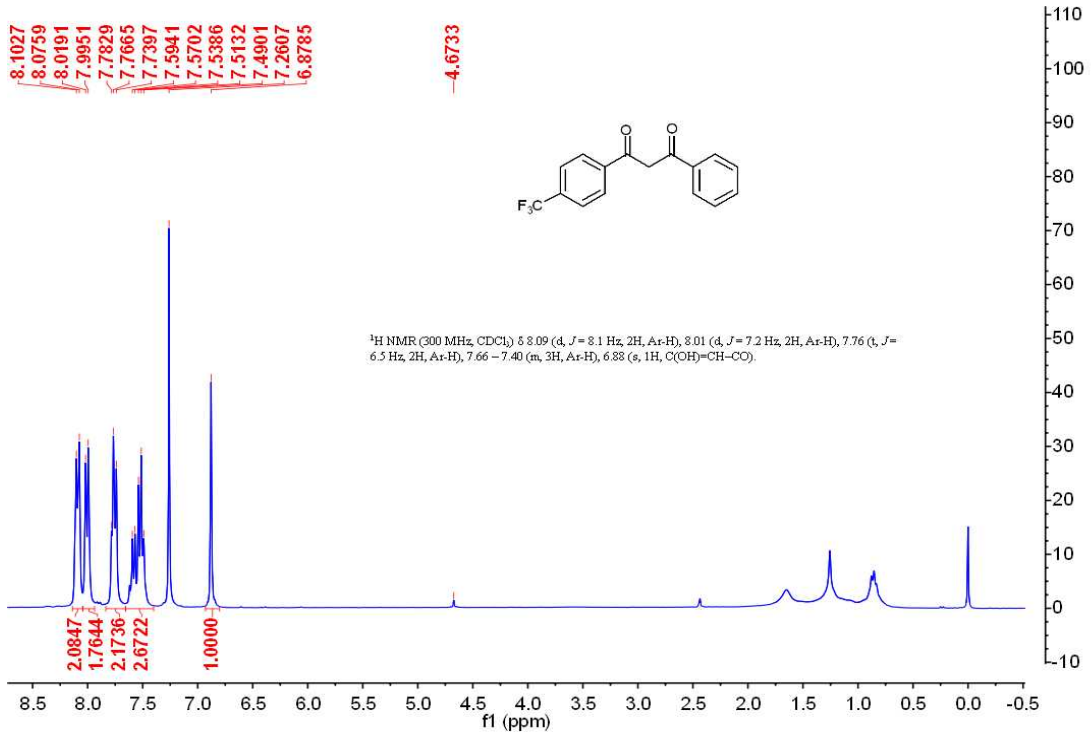
2e$_3$: 89 %, light yellow solid, m.p. 130–131 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.98 (d, *J* = 9.0 Hz, 4 H, Ar–H), 7.54–7.45 (m, 3 H, Ar–H), 6.97 (d, *J* = 8.8 Hz, 2 H, Ar–H), 6.79 (s, 1 H, C(OH)=CH–CO), 3.87 (s, 3 H, OCH_3). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55; O, 18.88. Found: C, 75.49; H, 5.50; O, 18.82. Mass (MS): m/z 255.1 $[M+H]^+$.



2f$_1$: 50 %, red-brown oil. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.94 (d, *J* = 7.2 Hz, 2 H, Ar–H), 7.77 (d, *J*= 7.3 Hz, 1 H, Ar–H), 7.68–7.51 (m, 4 H, Ar–H), 7.47 (t, *J* = 7.4 Hz, 2 H, Ar–H), 6.49 (s, 1 H, C(OH)=CH–CO). Anal. Calcd for $C_{16}H_{11}F_3O_2$: C, 65.76; H, 3.79; O, 10.95. Found: C, 65.65; H, 3.68; O, 10.84. Mass (MS): m/z 293.1 $[M+H]^+$.

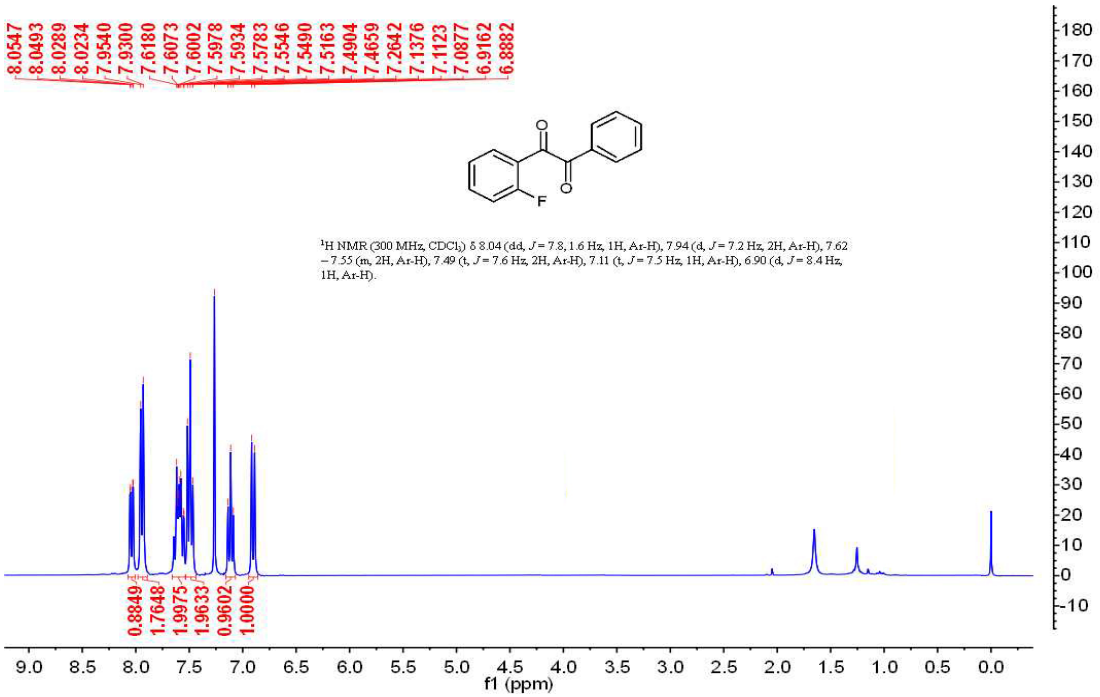


2f$_2$: 60 %, red oil. δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.23 (s, 1 H, Ar–H), 8.17 (d, *J* = 7.9 Hz, 1 H, Ar–H), 8.02 (d, *J* = 7.0 Hz, 2 H, Ar–H), 7.81 (d, *J* = 7.8 Hz, 1 H, Ar–H), 7.66–7.49 (m, 4 H, Ar–H), 6.88 (s, 1 H, C(OH)=CH–CO). Anal. Calcd for $C_{16}H_{11}F_3O_2$: C, 65.76; H, 3.79; O, 10.95. Found: C, 65.62; H, 3.69; O, 10.94. Mass (MS): m/z 293.1 $[M+H]^+$.

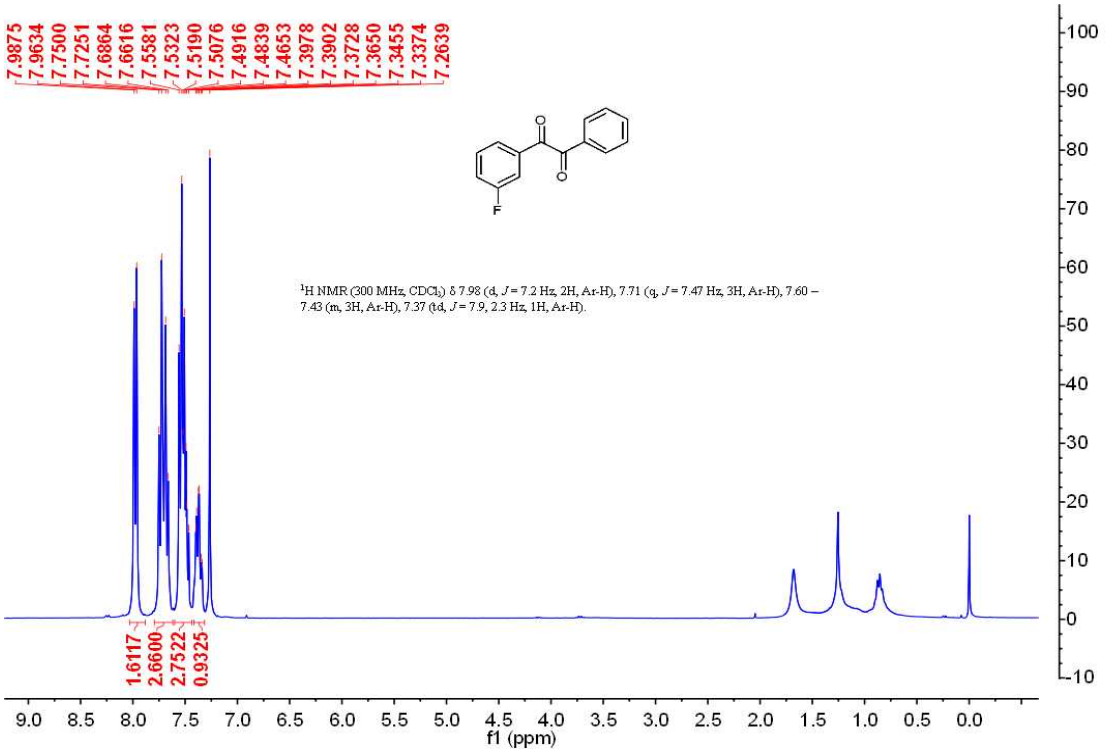


2f$_3$: 74 %, yellow solid. δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.09 (d, *J* = 8.1 Hz, 2 H, Ar–H), 8.01 (d, *J* = 7.2 Hz, 2 H, Ar–H), 7.76 (t, *J* = 6.5 Hz, 2 H, Ar–H), 7.66–7.40 (m, 3 H, Ar–H), 6.88 (s, 1 H, C(OH)=CH–CO). Anal. Calcd for $C_{16}H_{11}F_3O_2$: C, 65.76; H, 3.79; O, 10.95. Found: C, 65.66; H, 3.72; O, 10.89. Mass (MS): m/z 293.0 $[M+H]^+$.

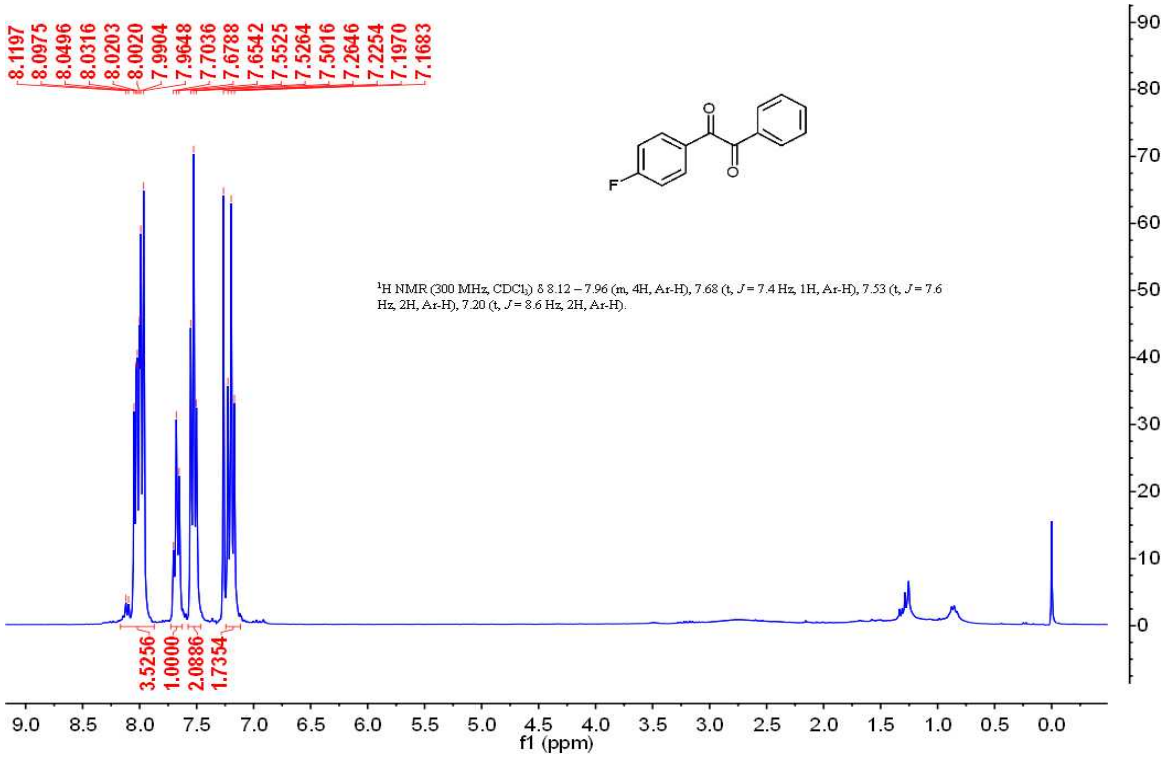
2. ^{1}H NMR spectra of 3a-f



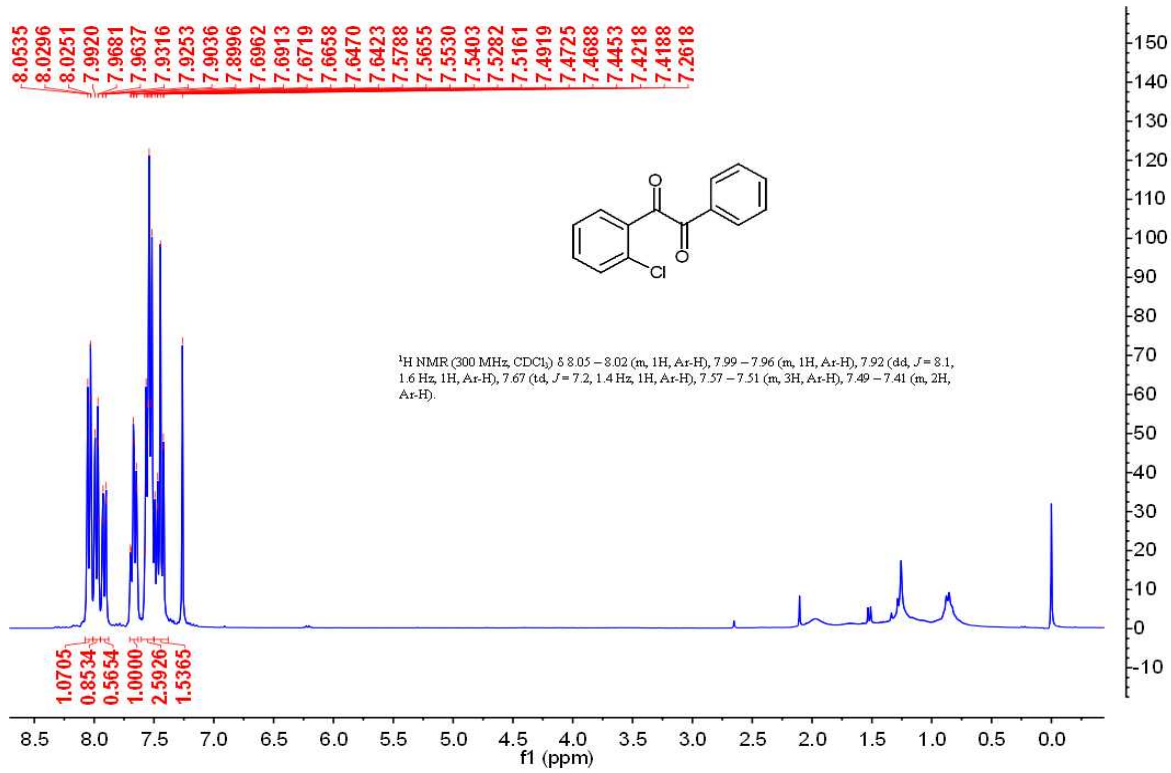
3a$_1$: 78 %, yellow solid, m.p. 58–60°C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.04 (dd, *J* = 7.8, 1.6 Hz, 1 H, Ar–H), 7.94 (d, *J* = 7.2 Hz, 2 H, Ar–H), 7.62–7.55 (m, 2 H, Ar–H), 7.49 (t, *J* = 7.6 Hz, 2 H, Ar–H), 7.11 (t, *J* = 7.5 Hz, 1 H, Ar–H), 6.90 (d, *J* = 8.4 Hz, 1 H, Ar–H). Anal. Calcd for $C_{14}H_9FO_2$: C, 73.68; H, 3.97; O, 14.02. Found: C, 73.67; H, 3.82; O, 14.08. Mass (MS): m/z 229.1 $[M+H]^+$.



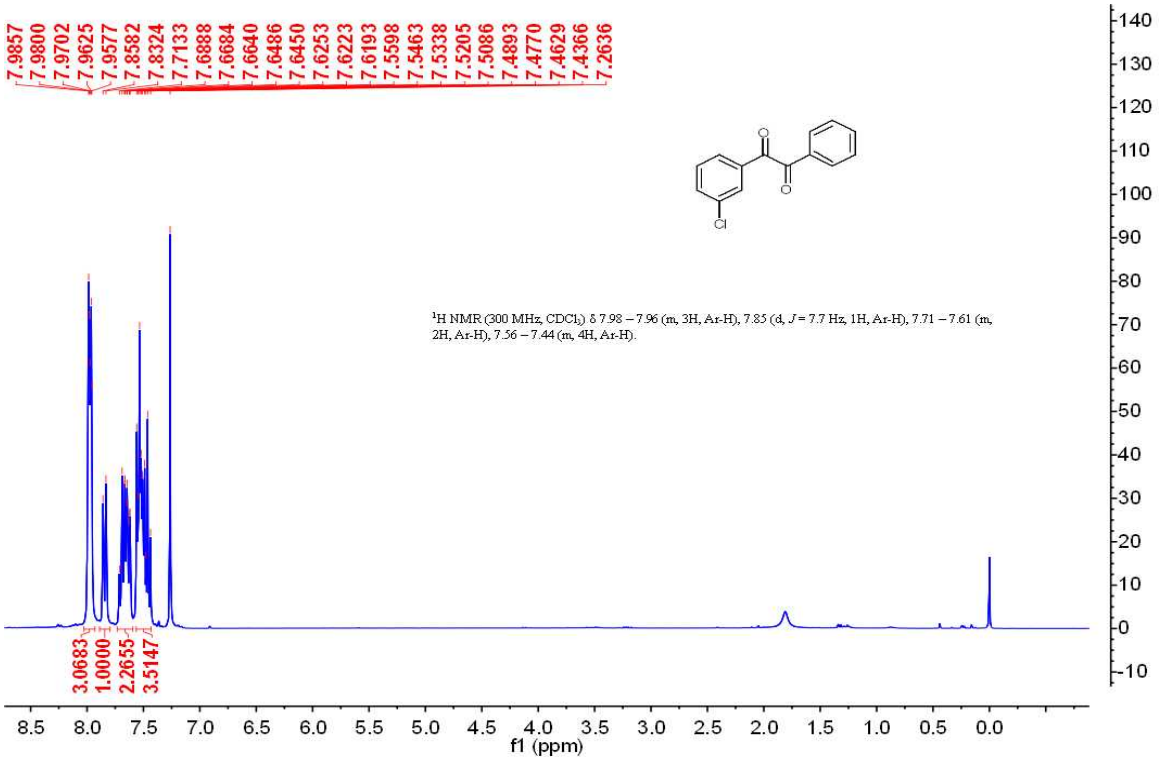
3a$_2$: 40 %, light yellow solid, m.p. 58–60°C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.98 (d, *J* = 7.2 Hz, 2 H, Ar–H), 7.71 (q, *J* = 7.47 Hz, 3 H, Ar–H), 7.60–7.43 (m, 3 H, Ar–H), 7.37 (m, 1 H, Ar–H). Anal. Calcd for $C_{14}H_9FO_2$: C, 73.68; H, 3.97; O, 14.02. Found: C, 73.60; H, 3.87; O, 13.97. Mass (MS): m/z 229.1 $[M+H]^+$.



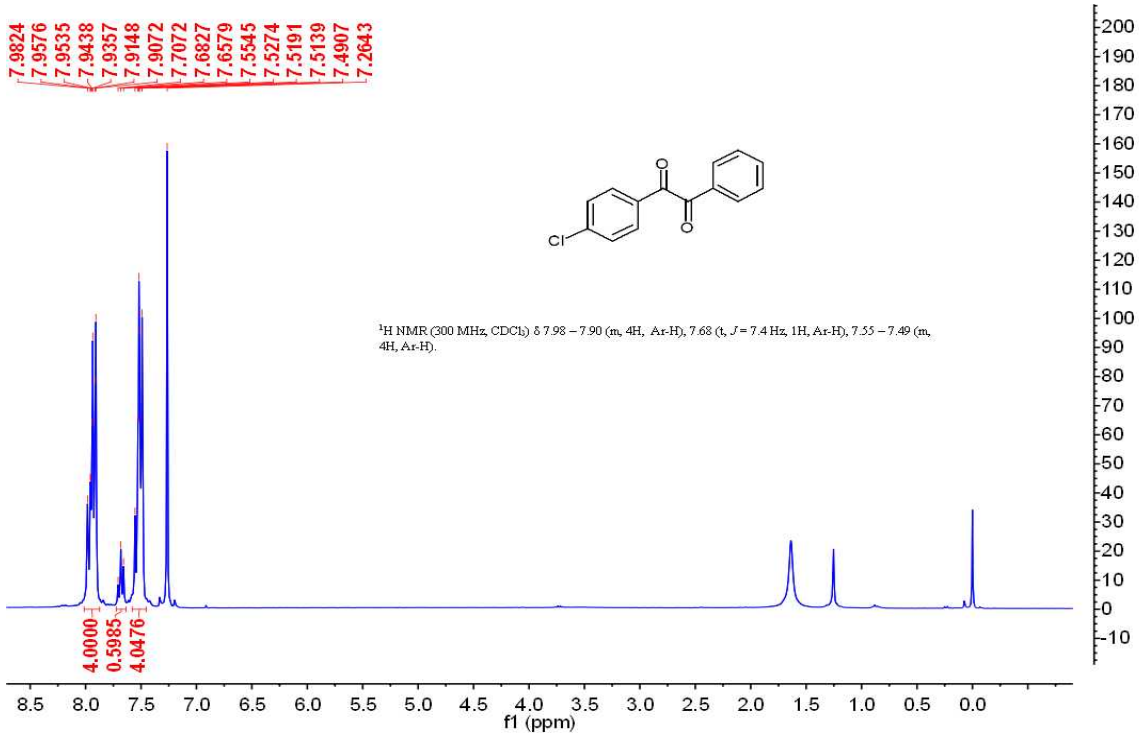
3a$_3$: 72 %, yellow solid, m.p. 62–63.5 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.12–7.96 (m, 4 H, Ar–H), 7.68 (t, *J* = 7.4 Hz, 1 H, Ar–H), 7.53 (t, *J* = 7.6 Hz, 2 H, Ar–H), 7.20 (m, 2 H, Ar–H). Anal. Calcd for $C_{14}H_9FO_2$: C, 73.68; H, 3.97; O, 14.02. Found: C, 73.62; H, 3.93; O, 13.99. Mass (MS): m/z 229.1 $[M+H]^+$.



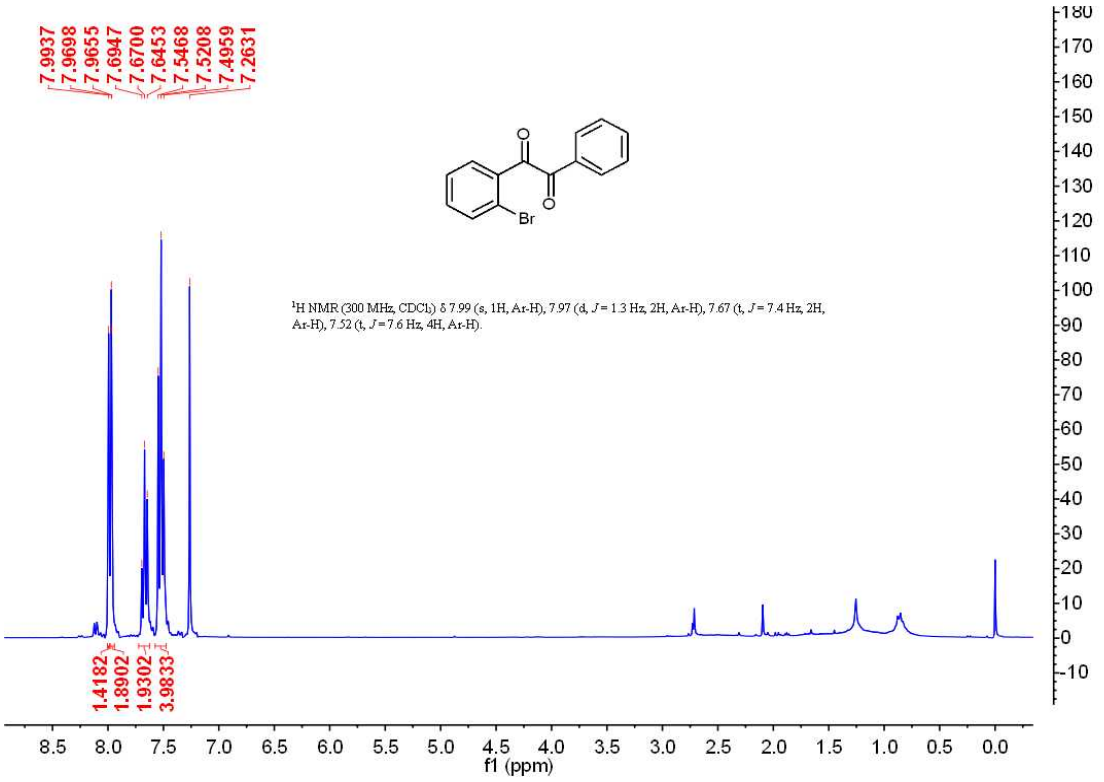
3b$_1$: 75 %, light yellow oil. δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.05-8.02 (m, 1 H, Ar–H), 7.99-7.96 (m, 1 H, Ar–H), 7.92 (dd, *J* = 8.1, 1.6 Hz, 1 H, Ar–H), 7.67 (td, *J* = 7.2, 1.4 Hz, 1 H, Ar–H), 7.57-7.51 (m, 3 H, Ar–H), 7.49–7.41 (m, 2 H, Ar–H). Anal. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71; O, 13.08. Found: C, 68.68; H, 3.69; O, 13.00. Mass (MS): m/z 245.0 $[M+H]^+$.



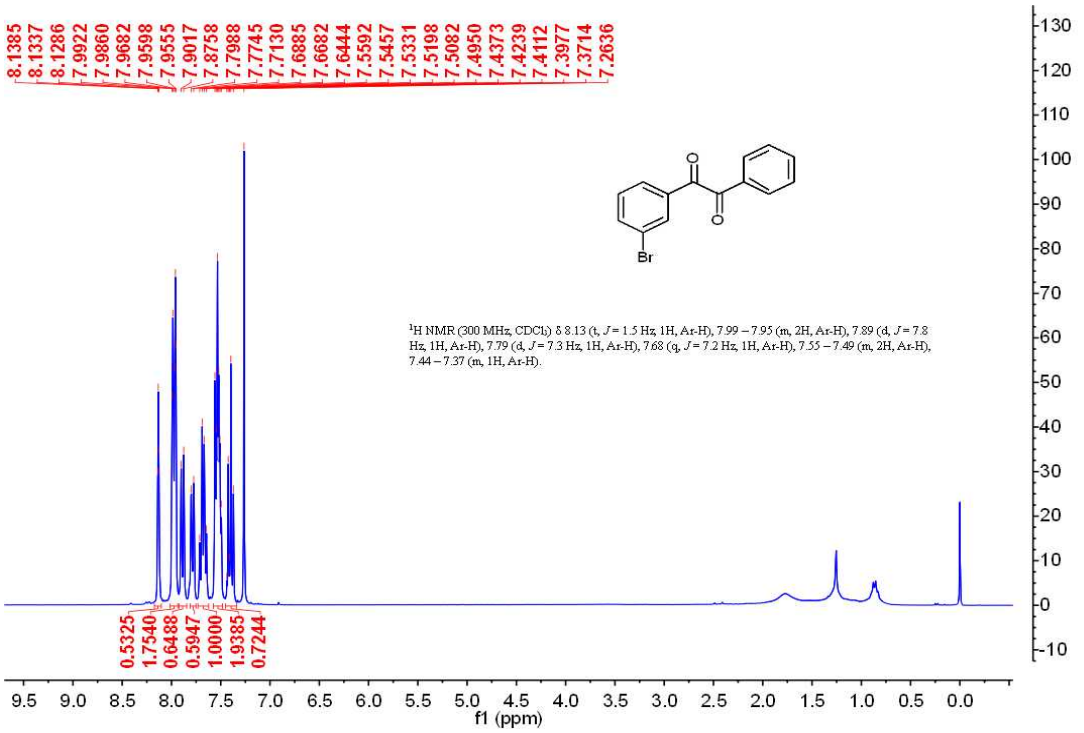
3b$_2$: 84 %, yellow solid, m.p. 89–99 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.98–7.96 (m, 3 H, Ar–H), 7.85 (d, *J* = 7.7 Hz, 1 H, Ar–H), 7.71–7.61 (m, 2 H, Ar–H), 7.56–7.44 (m, 4 H, Ar–H). Anal. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71; O, 13.08. Found: C, 68.65; H, 3.67; O, 13.01. Mass (MS): m/z 245.1 $[M+H]^+$.



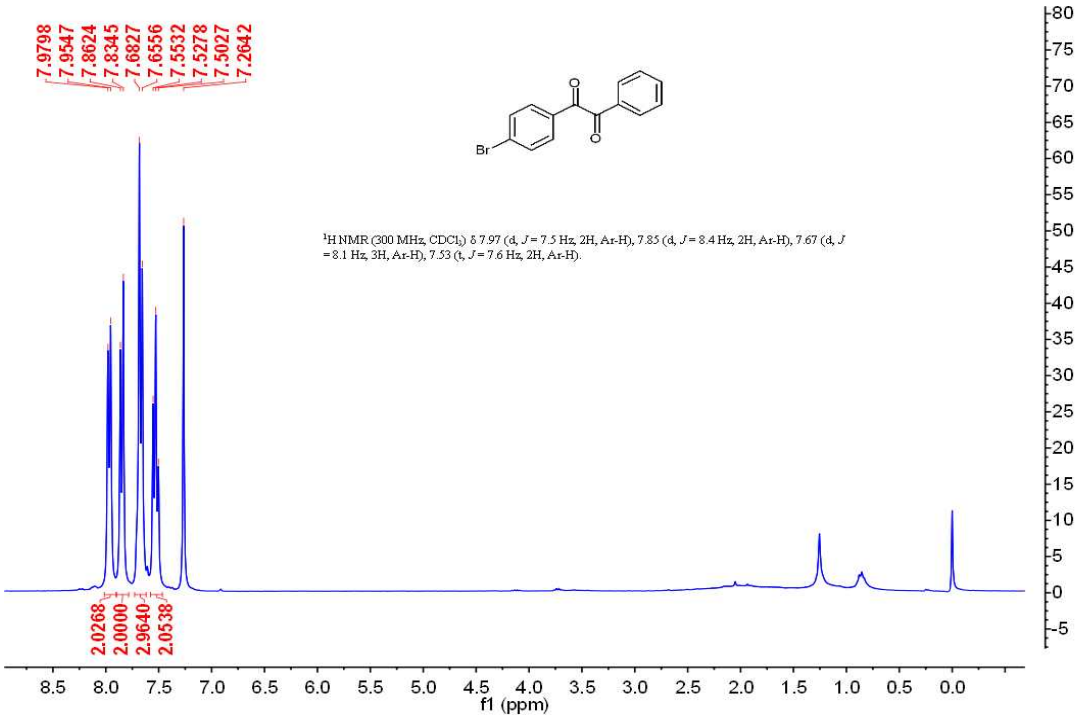
3b$_3$: 35 %, light yellow solid, m.p. 77.0–78.1 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.98–7.90 (m, 4 H, Ar–H), 7.68 (t, *J* = 7.4 Hz, 1 H, Ar–H), 7.55–7.49 (m, 4 H, Ar–H). Anal. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71; O, 13.08. Found: C, 68.70; H, 3.68; O, 13.05. Mass (MS): m/z 245.1 $[M+H]^+$.



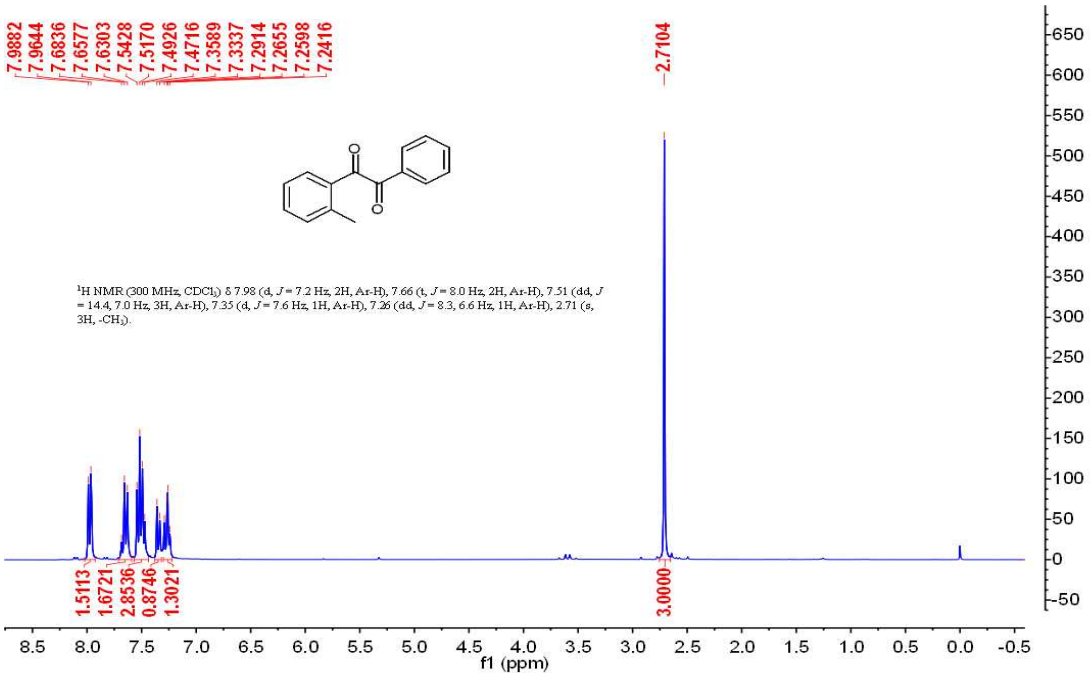
3c$_1$: 45 %, dark yellow solid; m.p. 40–41 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.97 (d, *J* = 7.2 Hz, 3 H, Ar–H), 7.67 (t, *J* = 7.4 Hz, 2 H, Ar–H), 7.52 (t, *J* = 7.6 Hz, 4 H, Ar–H). Anal. Calcd for $C_{14}H_9BrO_2$: C, 58.16; H, 3.14; O, 11.07. Found: C, 58.10; H, 3.08; O, 11.02. Mass (MS): m/z 289.0 $[M+H]^+$.



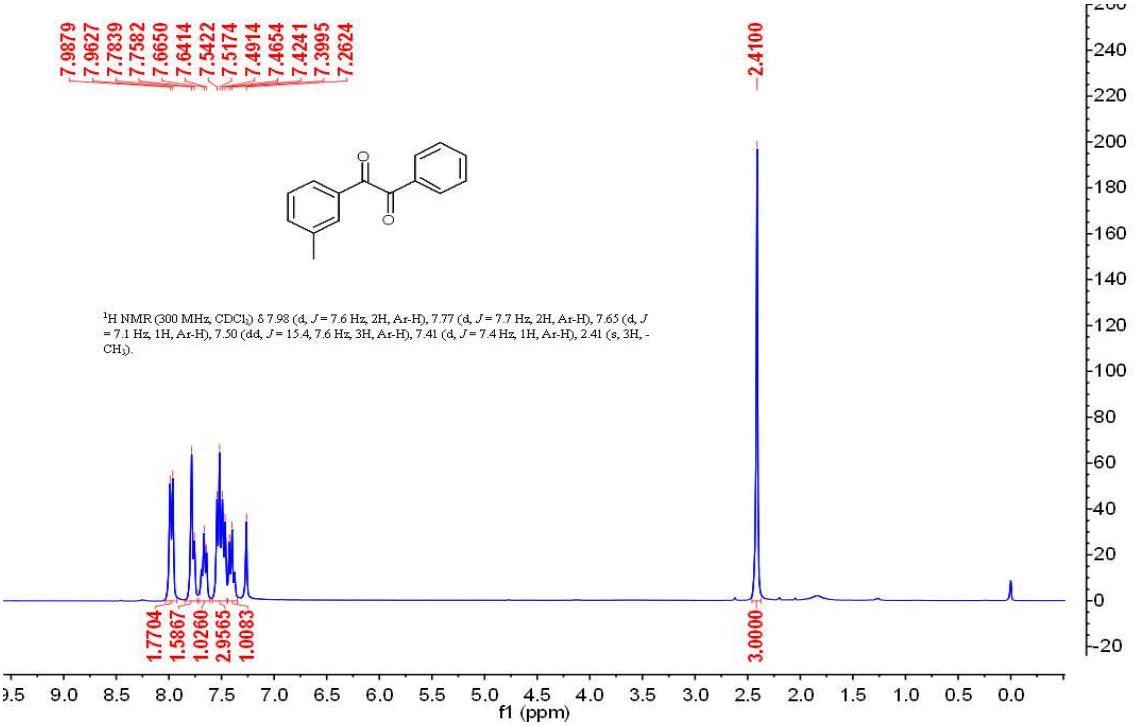
3c$_2$: 90 %, dark yellow solid, m.p. 80–81 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.13 (t, *J* = 1.5 Hz, 1H, Ar–H), 7.99–7.95 (m, 2 H, Ar–H), 7.89 (d, *J* = 7.8 Hz, 1 H, Ar–H), 7.79 (d, *J* = 7.3 Hz, 1 H, Ar–H), 7.68 (q, *J* = 7.2 Hz, 1 H, Ar–H), 7.55–7.49 (m, 2 H, Ar–H), 7.44–7.37 (m, 1 H, Ar–H). Anal. Calcd for $C_{14}H_9BrO_2$: C, 58.16; H, 3.14; O, 11.07. Found: C, 58.13; H, 3.10; O, 11.00. Mass (MS): m/z 288.9 $[M+H]^+$.



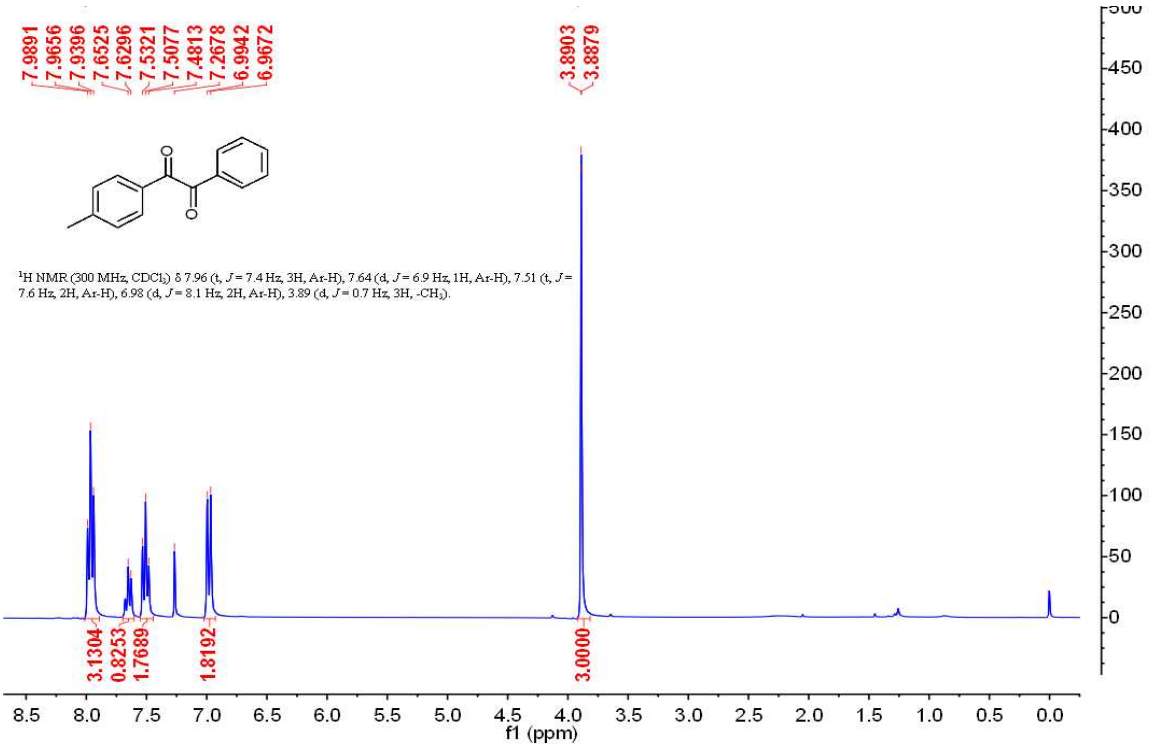
3c$_3$: 40 %, yellow solid, m.p. 86–87 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.97 (d, *J* = 7.5 Hz, 2 H, Ar–H), 7.85 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.67 (d, *J* = 8.1 Hz, 3 H, Ar–H), 7.53 (t, *J* = 7.6 Hz, 2 H, Ar–H). Anal. Calcd for $C_{14}H_9BrO_2$: C, 58.16; H, 3.14; O, 11.07. Found: C, 58.10; H, 3.08; O, 11.08. Mass (MS): m/z 288.9 $[M+H]^+$.



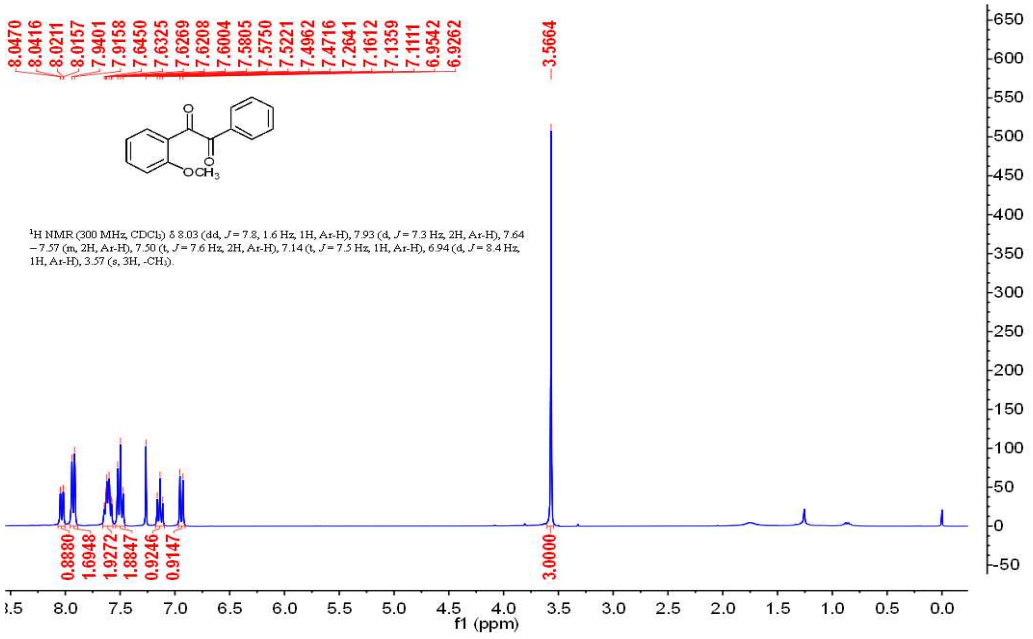
3d$_1$: 69 %, light yellow solid, m.p. 56–57 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.98 (d, *J* = 7.2 Hz, 2 H, Ar–H), 7.66 (t, *J* = 8.0 Hz, 2 H, Ar–H), 7.51 (dd, *J* = 14.4, 7.0 Hz, 3 H, Ar–H), 7.35 (d, *J* = 7.6 Hz, 1 H, Ar–H), 7.26 (dd, *J* = 8.3, 6.6 Hz, 1 H, Ar–H), 2.71 (s, 3 H, CH_3). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39; O, 14.27. Found: C, 80.29; H, 5.31; O, 14.28. Mass (MS): m/z 225.1 $[M+H]^+$.



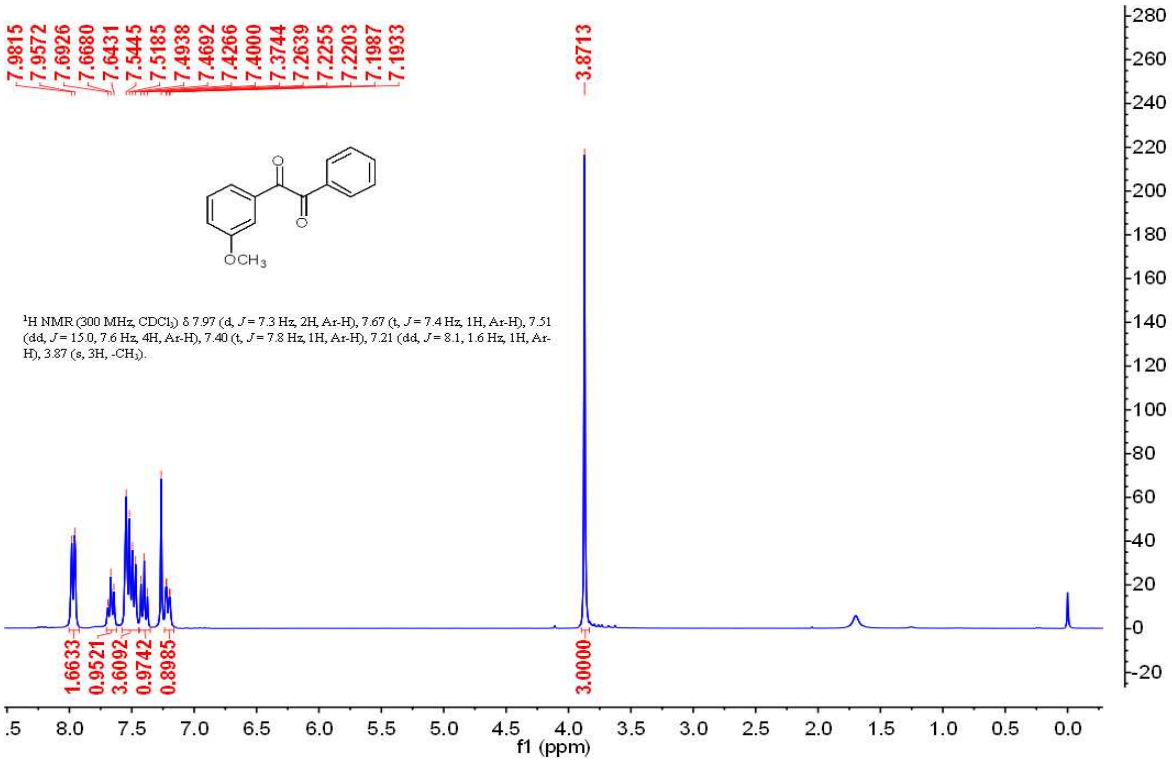
3d$_2$: 82 %, yellow solid, m.p. 56–57 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.98 (d, *J* = 7.6 Hz, 2 H, Ar–H), 7.77 (d, *J* = 7.7 Hz, 2 H, Ar–H), 7.65 (d, *J* = 7.1 Hz, 1 H, Ar–H), 7.50 (dd, *J* = 15.4, 7.6 Hz, 3 H, Ar–H), 7.41 (d, *J* = 7.4 Hz, 1 H, Ar–H), 2.41 (s, 3 H, CH_3). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39; O, 14.27. Found: C, 80.32; H, 5.37; O, 14.30. Mass (MS): m/z 225.0 $[M+H]^+$.



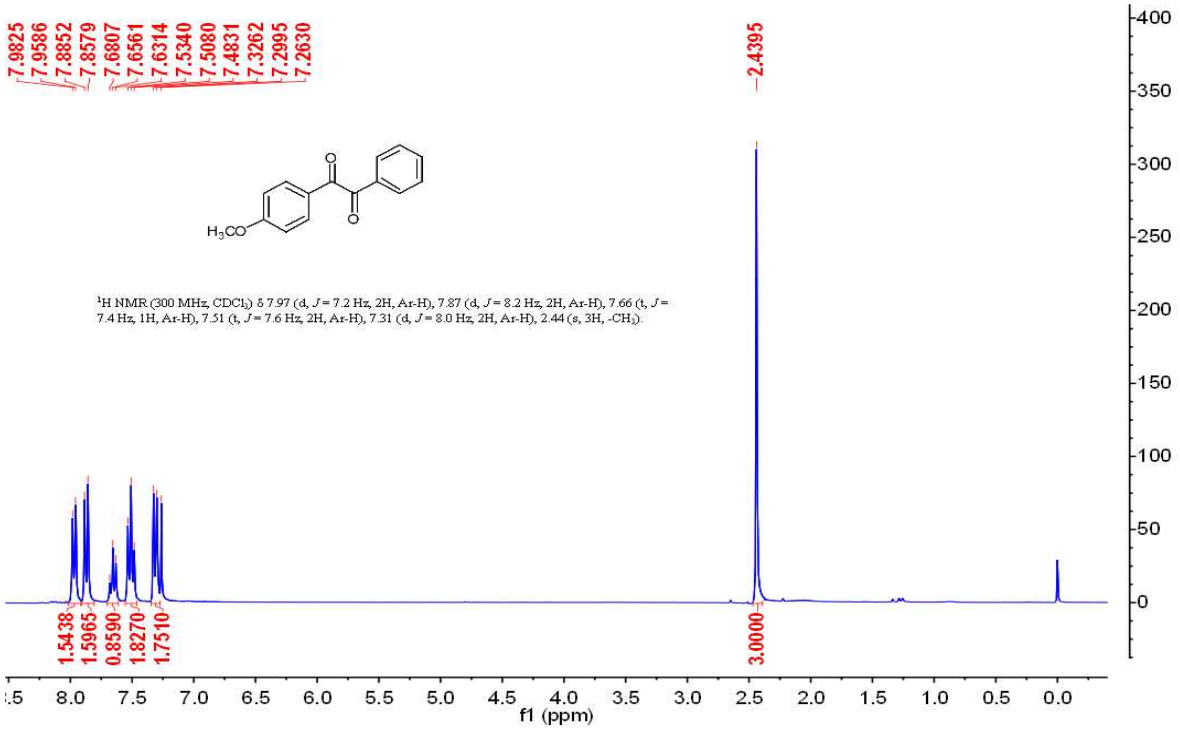
3d$_3$: 70 %, light yellow oil. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.96 (t, *J* = 7.4 Hz, 3 H, Ar–H), 7.64 (d, *J* = 6.9 Hz, 1 H, Ar–H), 7.51 (t, *J* = 7.6 Hz, 2 H, Ar–H), 6.98 (d, *J* = 8.1 Hz, 2 H, Ar–H), 3.89 (d, *J* = 0.7 Hz, 3 H, CH_3). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39; O, 14.27. Found: C, 80.28; H, 5.27; O, 14.25. Mass (MS): m/z 225.1 $[M+H]^+$.



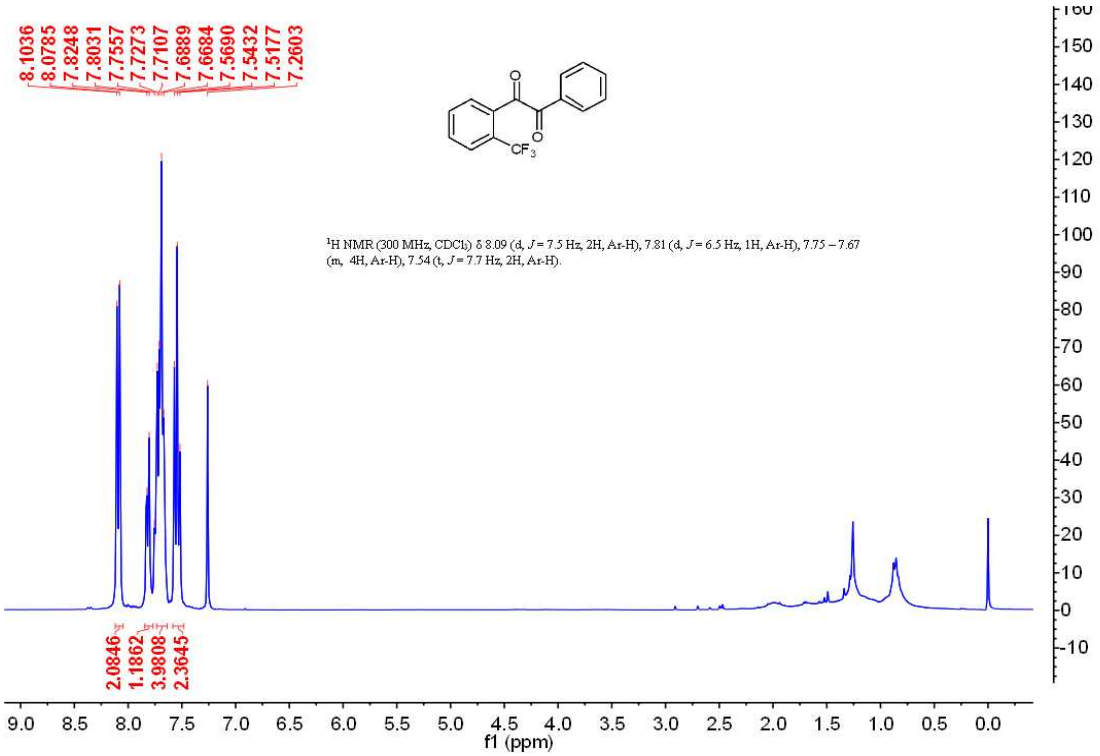
3e$_1$: 75 %, red-brown solid, m.p. 71–72 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.03 (dd, *J* = 7.8, 1.6 Hz, 1 H, Ar–H), 7.93 (d, *J* = 7.3 Hz, 2 H, Ar–H), 7.64–7.57 (m, 2 H, Ar–H), 7.50 (t, *J* = 7.6 Hz, 2 H, Ar–H), 7.14 (t, *J* = 7.5 Hz, 1 H, Ar–H), 6.94 (d, *J* = 8.4 Hz, 1 H, Ar–H), 3.57 (s, 3 H, OCH_3). Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03; O, 19.98. Found: C, 74.91; H, 4.97; O, 19.75. Mass (MS): m/z 241.1 $[M+H]^+$.



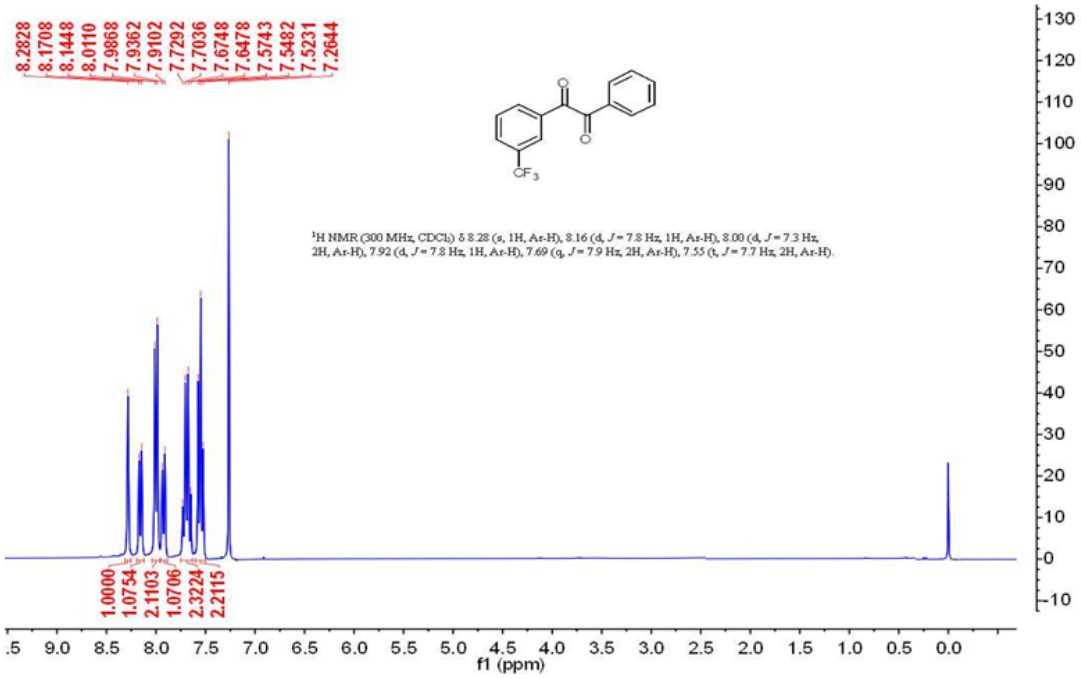
3e$_2$: 87 %, yellow solid, m.p. 91–93°C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.97 (d, *J* = 7.3 Hz, 2 H, Ar–H), 7.67 (t, *J* = 7.4 Hz, 1 H, Ar–H), 7.51 (dd, *J* = 15.0, 7.6 Hz, 4 H, Ar–H), 7.40 (t, *J* = 7.8 Hz, 1 H, Ar–H), 7.21 (dd, *J* = 8.1, 1.6 Hz, 1 H, Ar–H), 3.87 (s, 3 H, OCH_3). Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03; O, 19.98. Found: C, 74.89; H, 4.89; O, 19.84. Mass (MS): m/z 241.1 $[M+H]^+$.



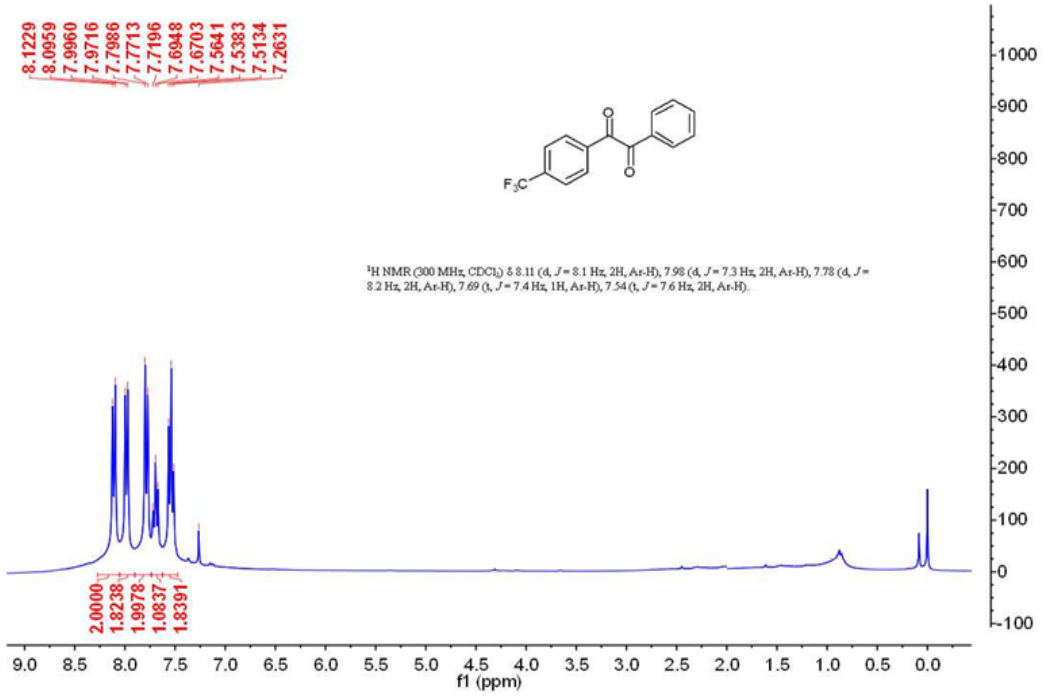
3e$_3$: 80 %, light yellow oil. δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.97 (d, *J* = 7.2 Hz, 2 H, Ar–H), 7.87 (d, *J* = 8.2 Hz, 2 H, Ar–H), 7.66 (t, *J* = 7.4 Hz, 1 H, Ar–H), 7.51 (t, *J* = 7.6 Hz, 2 H, Ar–H), 7.31 (d, *J* = 8.0 Hz, 2 H, Ar–H), 2.44 (s, 3 H, CH_3). Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03; O, 19.98. Found: C, 74.92; H, 4.93; O, 19.94. Mass (MS): m/z 241.1 $[M+H]^+$.



3f$_1$: 82 %, light yellow oil. δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.09 (d, *J* = 7.5 Hz, 2 H, Ar–H), 7.81 (d, *J* = 6.5 Hz, 1 H, Ar–H), 7.75 –7.67 (m, 4 H, Ar–H), 7.54 (t, *J* = 7.7 Hz, 2 H, Ar–H). Anal. Calcd for $C_{15}H_9F_3O_2$: C, 64.75; H, 3.26; O, 11.50. Found: C, 64.63; H, 3.19; O, 11.49. Mass (MS): m/z 279.1 $[M+H]^+$.

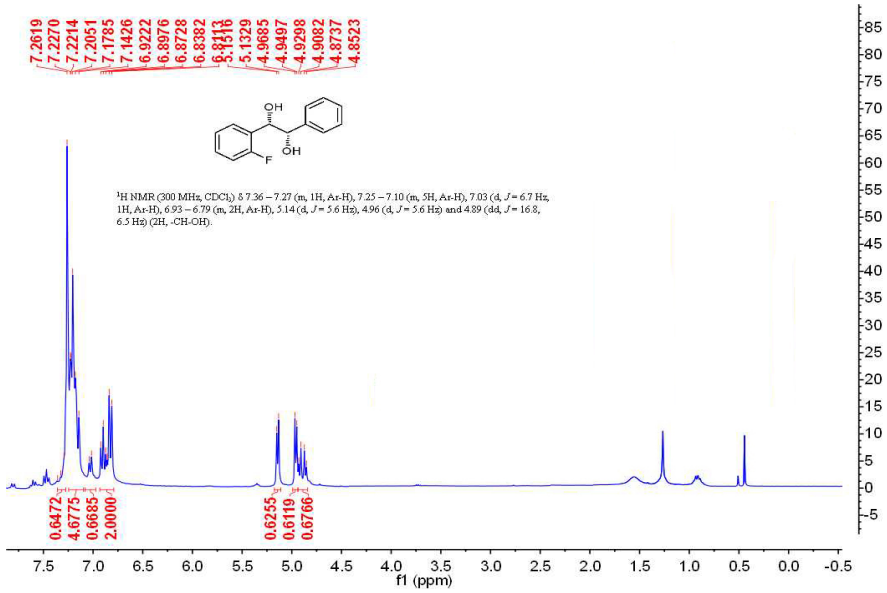


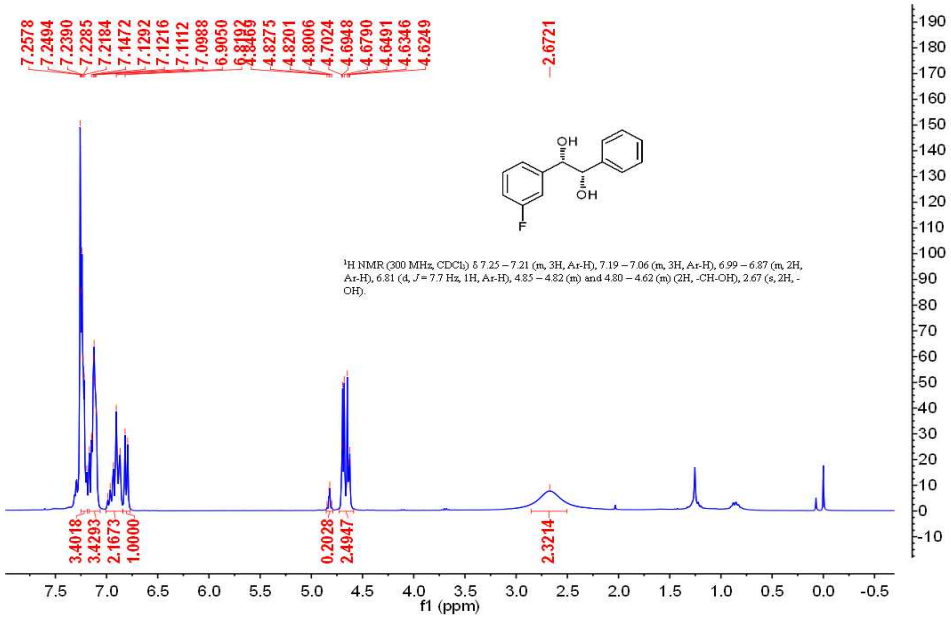
3f$_2$: 50 %, yellow solid, m.p. 69-70 °C. δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.28 (s, 1 H, Ar–H), 8.16 (d, *J* = 7.8 Hz, 1 H, Ar–H), 8.00 (d, *J* = 7.3 Hz, 2 H, Ar–H), 7.92 (d, *J* = 7.8 Hz, 1 H, Ar–H), 7.69 (q, *J* = 7.9 Hz, 2 H, Ar–H), 7.55 (t, *J* = 7.7 Hz, 2 H, Ar–H). Anal. Calcd for $C_{15}H_9F_3O_2$: C, 64.75; H, 3.26; O, 11.50. Found: C, 64.73; H, 3.21; O, 11.53. Mass (MS): m/z 279.1 $[M+H]^+$.

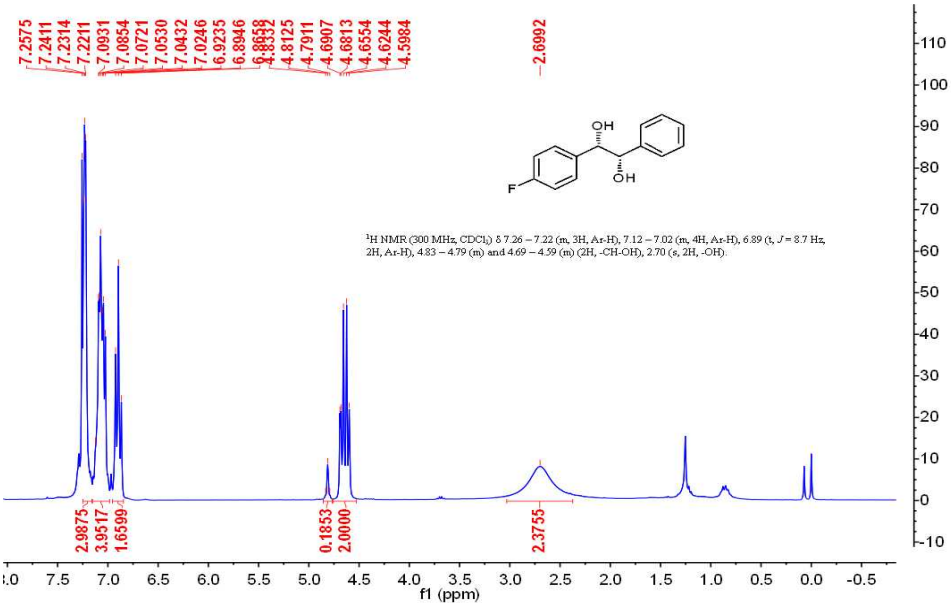


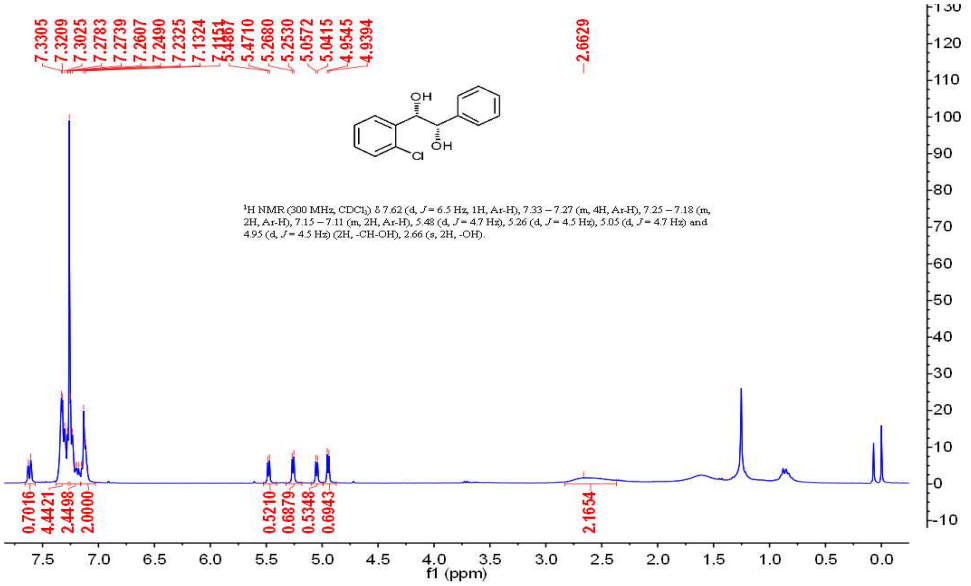
3f$_3$: 70 %, light yellow solid, m.p. 69-70 °C . δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.11 (d, *J* = 8.1 Hz, 2 H, Ar–H), 7.98 (d, *J* = 7.3 Hz, 2 H, Ar–H), 7.78 (d, *J* = 8.2 Hz, 2 H, Ar–H), 7.69 (t, *J* = 7.4 Hz, 1 H, Ar–H), 7.54 (t, *J* = 7.6 Hz, 2 H, Ar–H). Anal. Calcd for $C_{15}H_9F_3O_2$: C, 64.75; H, 3.26; O, 11.50. Found: C, 64.68; H, 3.23; O, 11.45. Mass (MS): m/z 279.1 $[M+H]^+$.

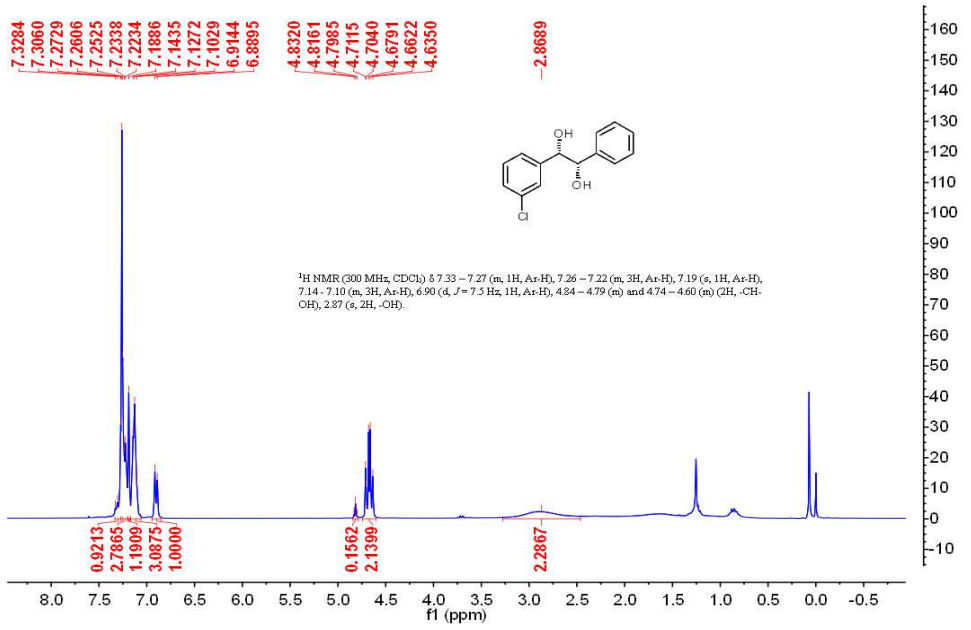
3. ^{1}H NMR spectra of 6a-f

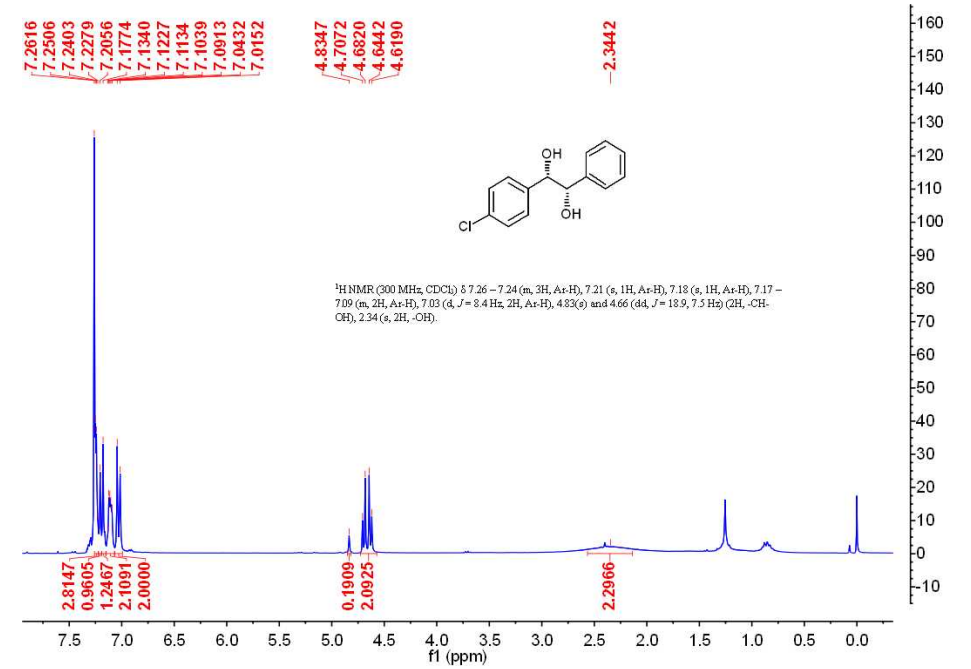


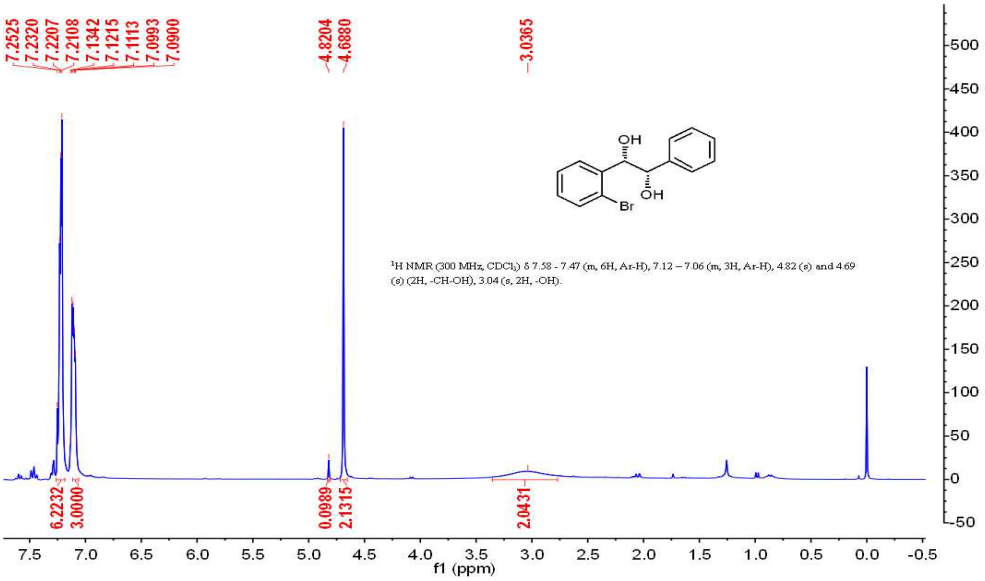




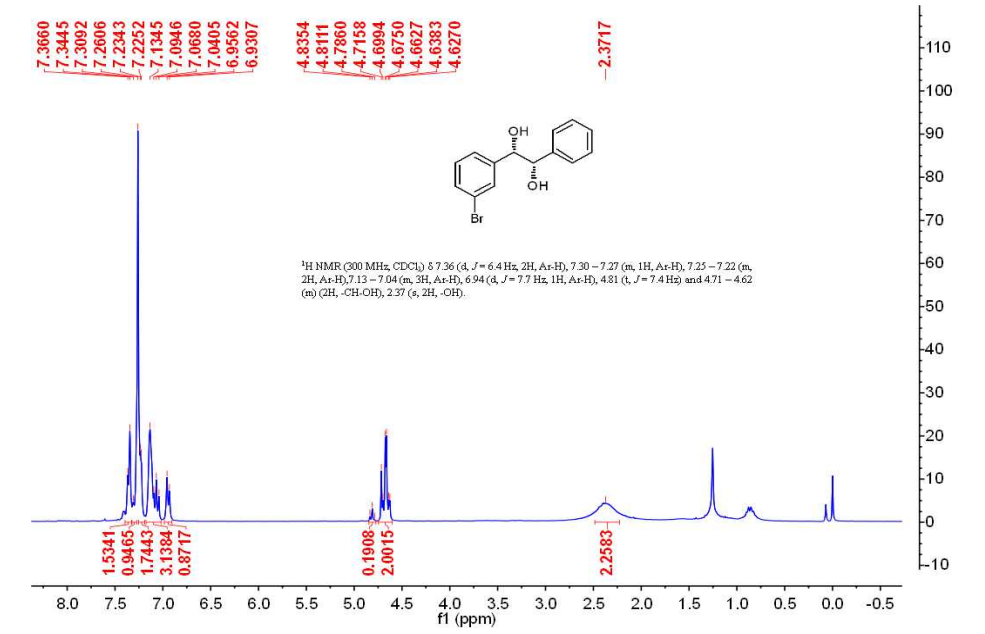




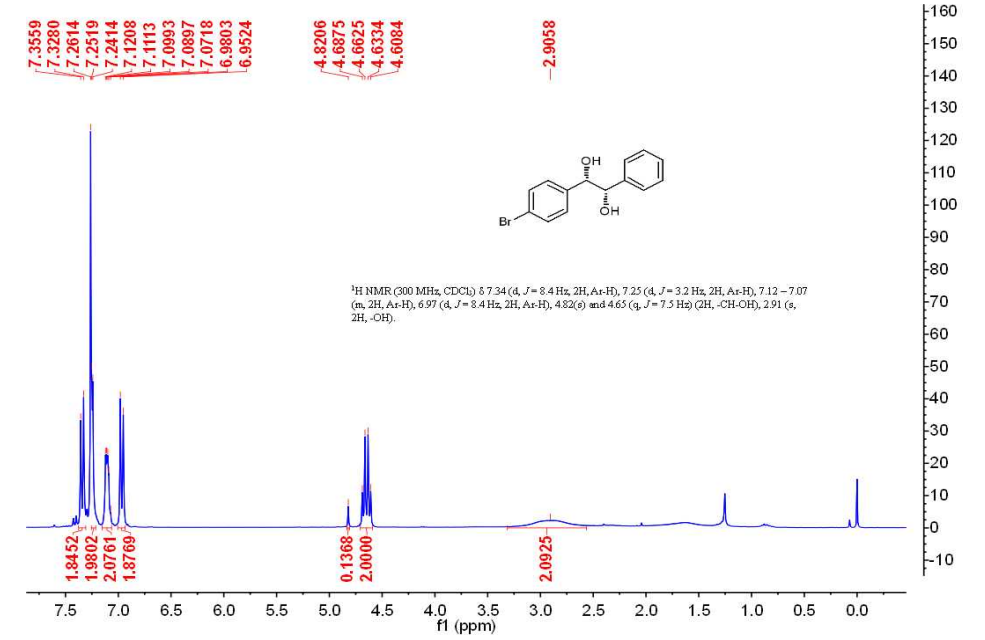




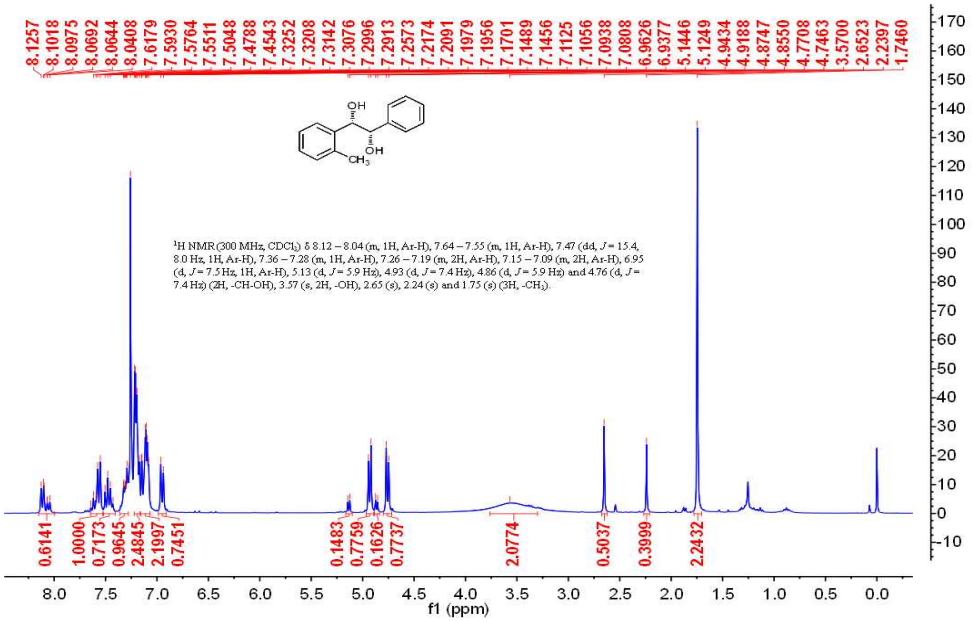
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 - 7.47 (m, 6H, Ar-H), 7.12 – 7.06 (m, 3H, Ar-H), 4.82 (s) and 4.69 (s) (2H, -CH-OH), 3.04 (s, 2H, -OH).

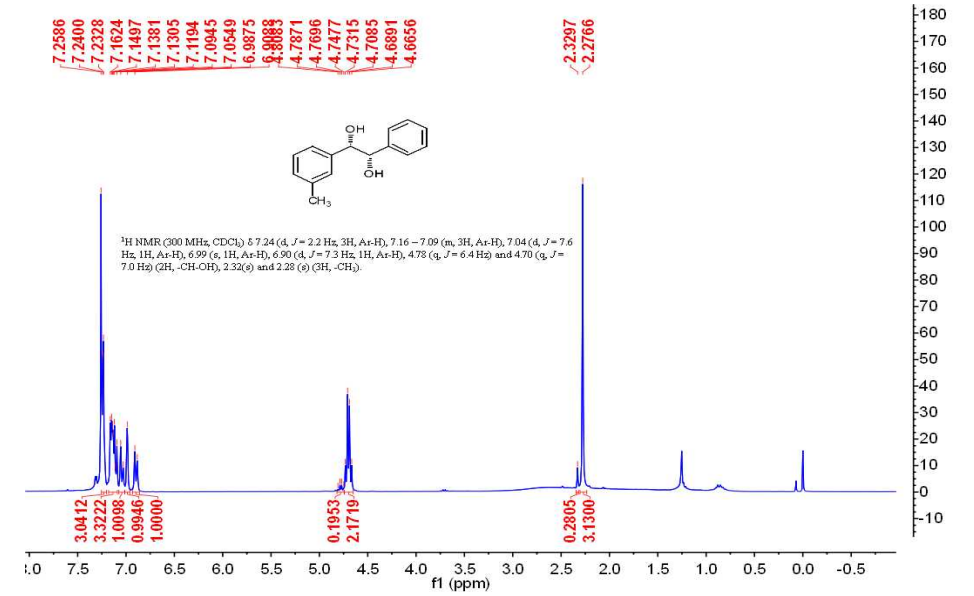


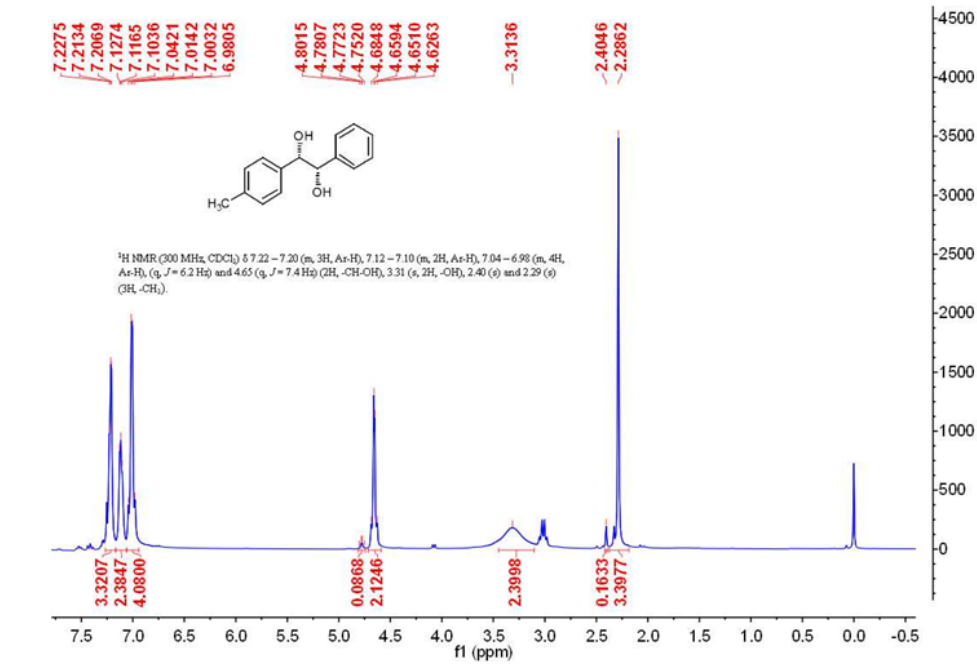
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, J = 6.4 Hz, 2H, Ar-H), 7.30 – 7.27 (m, 1H, Ar-H), 7.25 – 7.22 (m, 2H, Ar-H),7.13 – 7.04 (m, 3H, Ar-H), 6.94 (d, J = 7.7 Hz, 1H, Ar-H), 4.81 (t, J = 7.4 Hz) and 4.71 – 4.62 (m) (2H, -CH-OH), 2.37 (s, 2H, -OH).

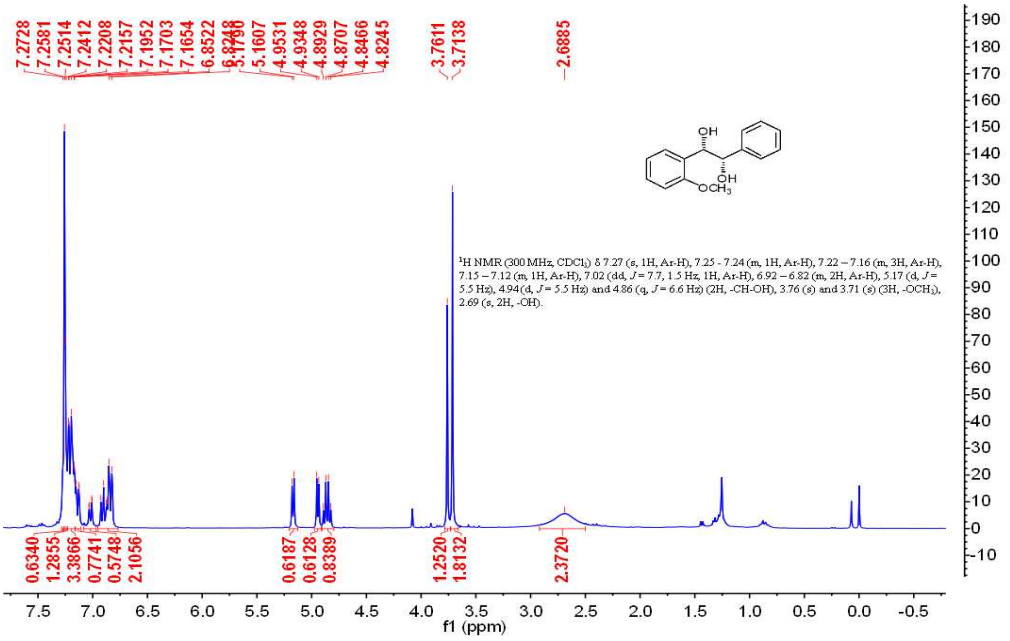


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, J = 8.4 Hz, 2H, Ar-H), 7.25 (d, J = 3.2 Hz, 2H, Ar-H), 7.12 – 7.07 (m, 2H, Ar-H), 6.97 (d, J = 8.4 Hz, 2H, Ar-H), 4.82(s) and 4.65 (q, J = 7.5 Hz) (2H, -CH-OH), 2.91 (s, 2H, -OH).

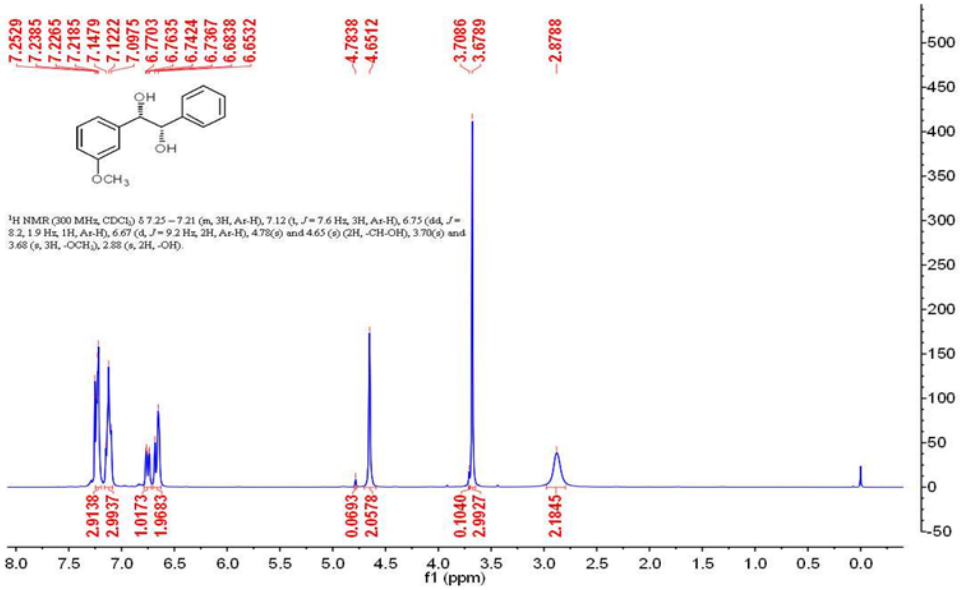




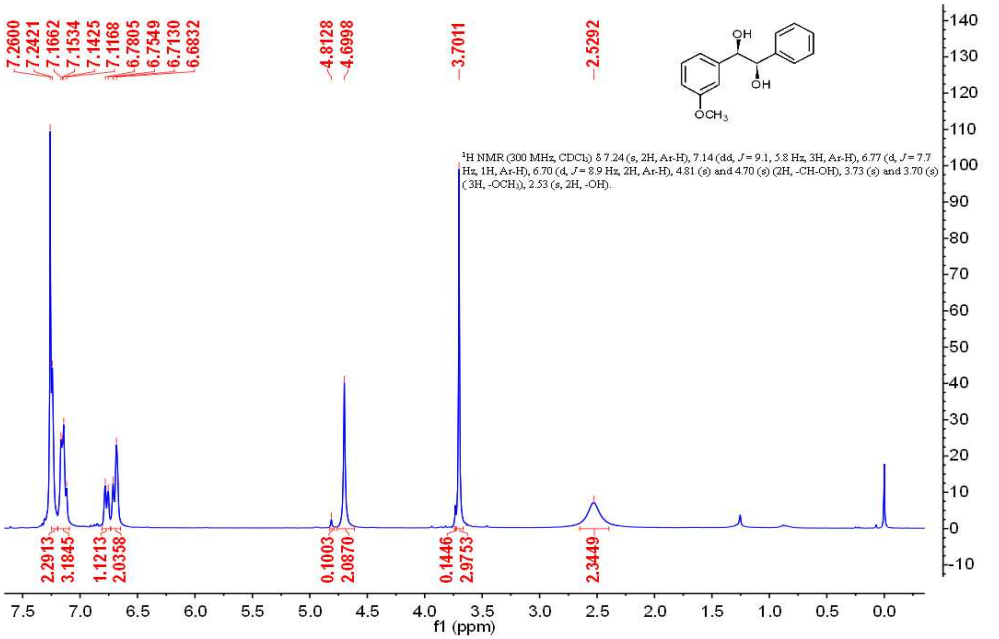




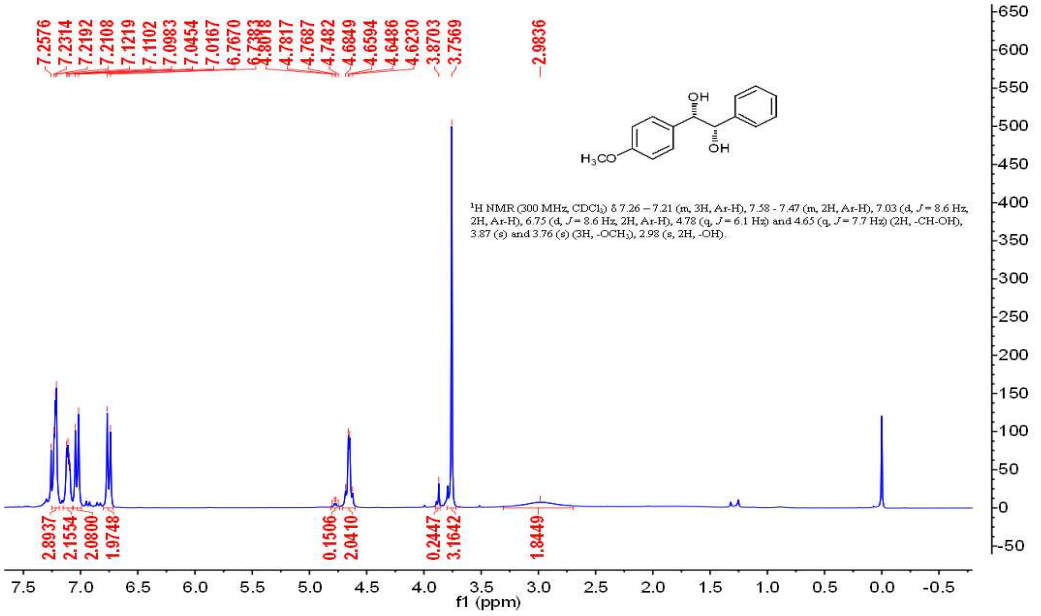
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (s, 1H, Ar-H), 7.25 - 7.24 (m, 1H, Ar-H), 7.22 – 7.16 (m, 3H, Ar-H), 7.15 – 7.12 (m, 1H, Ar-H), 7.02 (dd, *J* = 7.7, 1.5 Hz, 1H, Ar-H), 6.92 – 6.82 (m, 2H, Ar-H), 5.17 (d, *J* = 5.5 Hz), 4.94 (d, *J* = 5.5 Hz) and 4.86 (q, *J* = 6.6 Hz) (2H, -CH-OH), 3.76 (s) and 3.71 (s) (3H, $-OCH_3$), 2.69 (s, 2H, -OH).

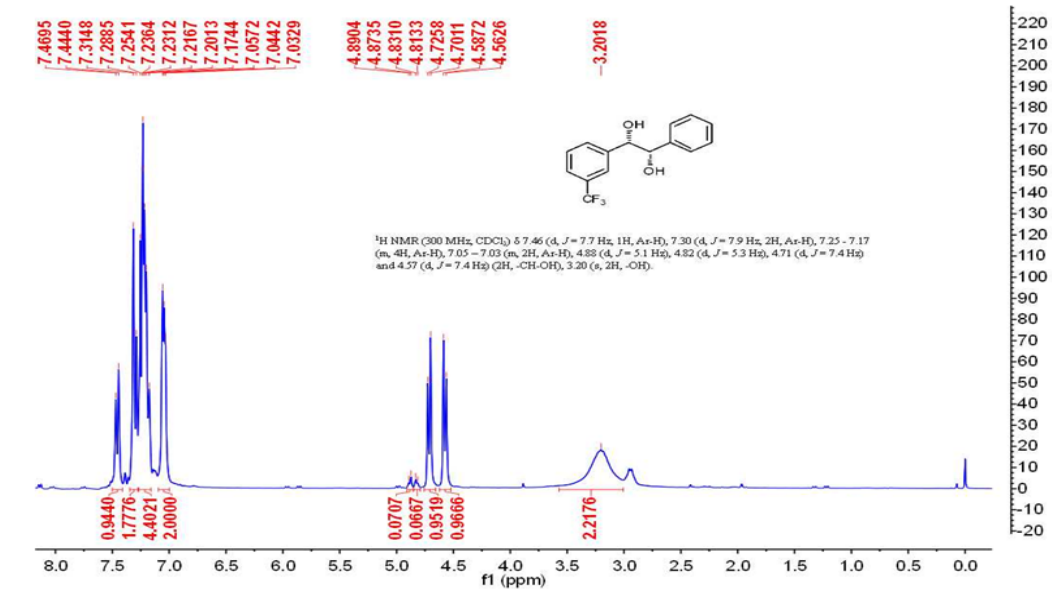


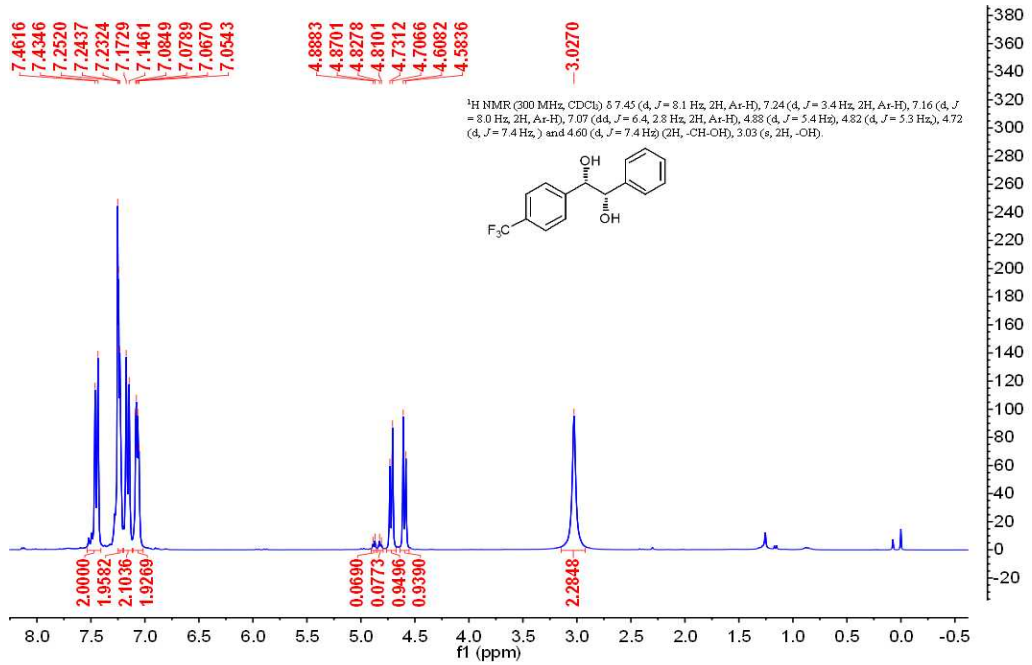
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 3H, Ar-H), 7.12 (t, *J* = 7.6 Hz, 3H, Ar-H), 6.75 (dd, *J* = 8.2, 1.9 Hz, 1H, Ar-H), 6.67 (d, *J* = 9.2 Hz, 2H, Ar-H), 4.78(s) and 4.65 (s) (2H, -CH-OH), 3.70(s) and 3.68 (s, 3H, $-OCH_3$), 2.88 (s, 2H, -OH).



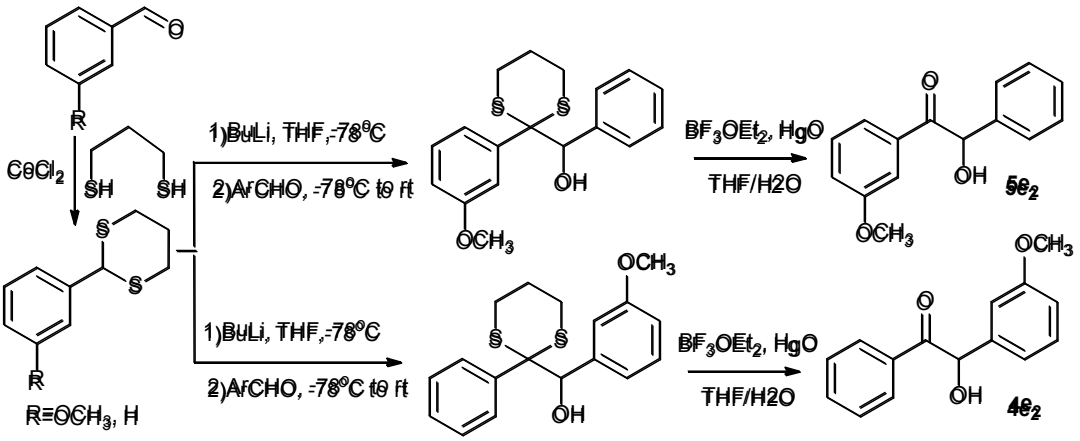
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (s, 2H, Ar-H), 7.14 (dd, *J* = 9.1, 5.8 Hz, 3H, Ar-H), 6.77 (d, *J* = 7.7 Hz, 1H, Ar-H), 6.70 (d, *J* = 8.9 Hz, 2H, Ar-H), 4.81 (s) and 4.70 (s) (2H, -CH-OH), 3.73 (s) and 3.70 (s) (3H, $-OCH_3$), 2.53 (s, 2H, -OH).

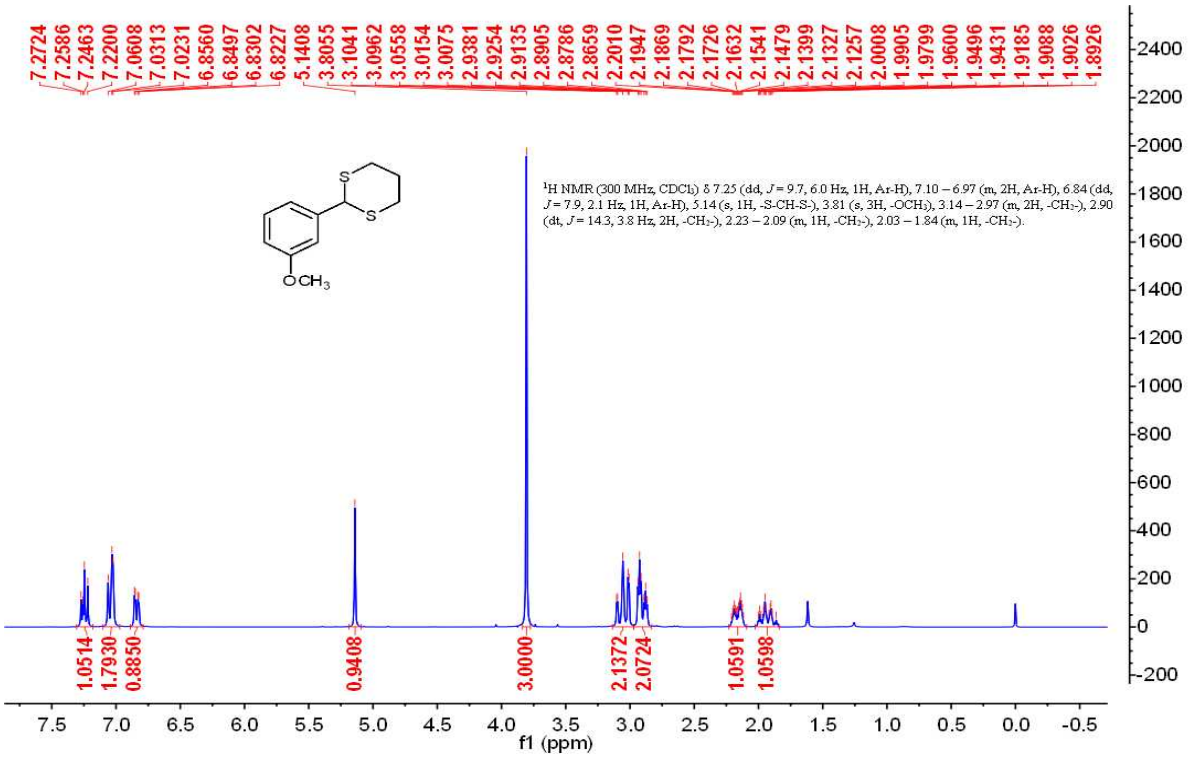


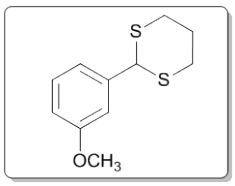




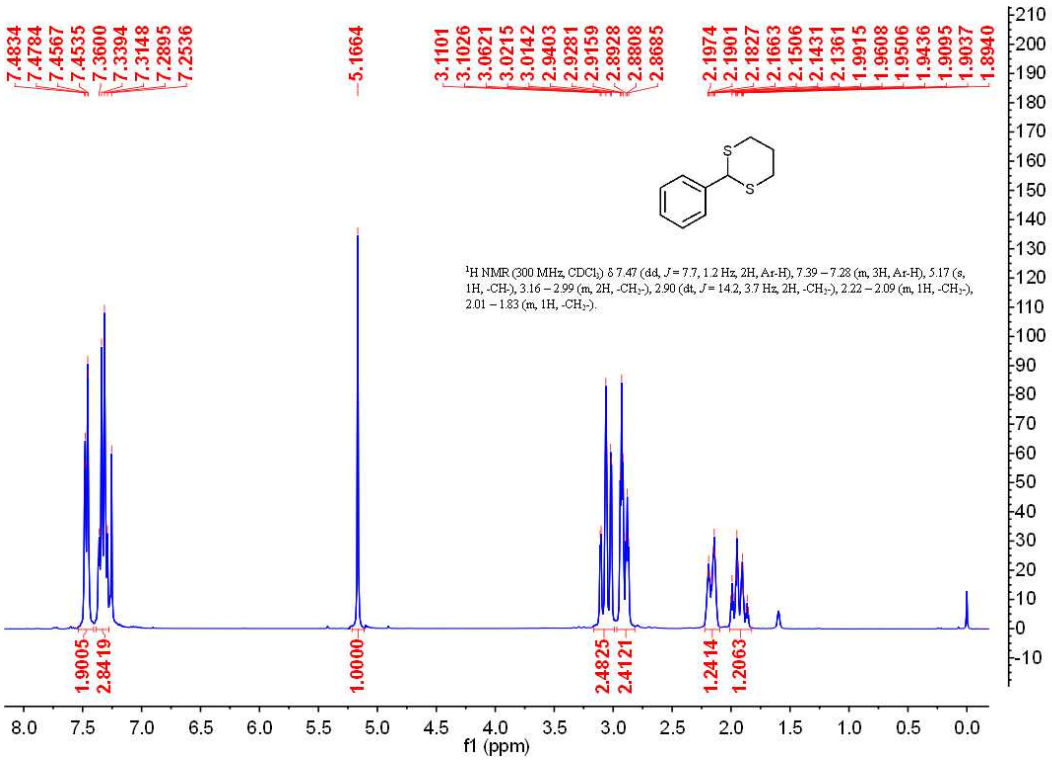
4. ^{1}H NMR spectra of reference materials $4e_2$, $5e_2$ and their intermediates

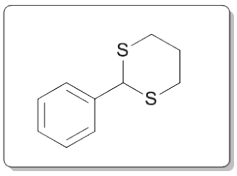




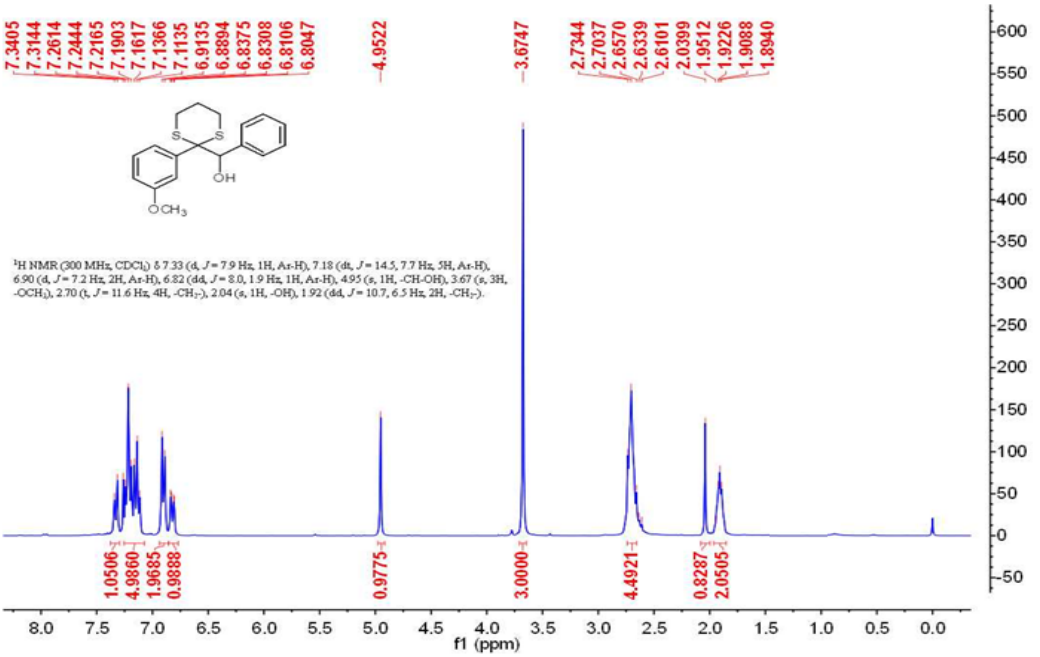


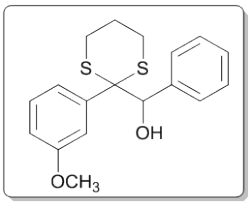
80% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 9.7, 6.0 Hz, 1H, Ar-H), 7.10 – 6.97 (m, 2H, Ar-H), 6.84 (dd, *J* = 7.9, 2.1 Hz, 1H, Ar-H), 5.14 (s, 1H, -CH-), 3.81 (s, 3H, -OCH_3), 3.14 – 2.97 (m, 2H, -CH_2-), 2.90 (dt, *J* = 14.3, 3.8 Hz, 2H, -CH_2-), 2.23 – 2.09 (m, 1H, -CH_2-), 2.03 – 1.84 (m, 1H, -CH_2-).



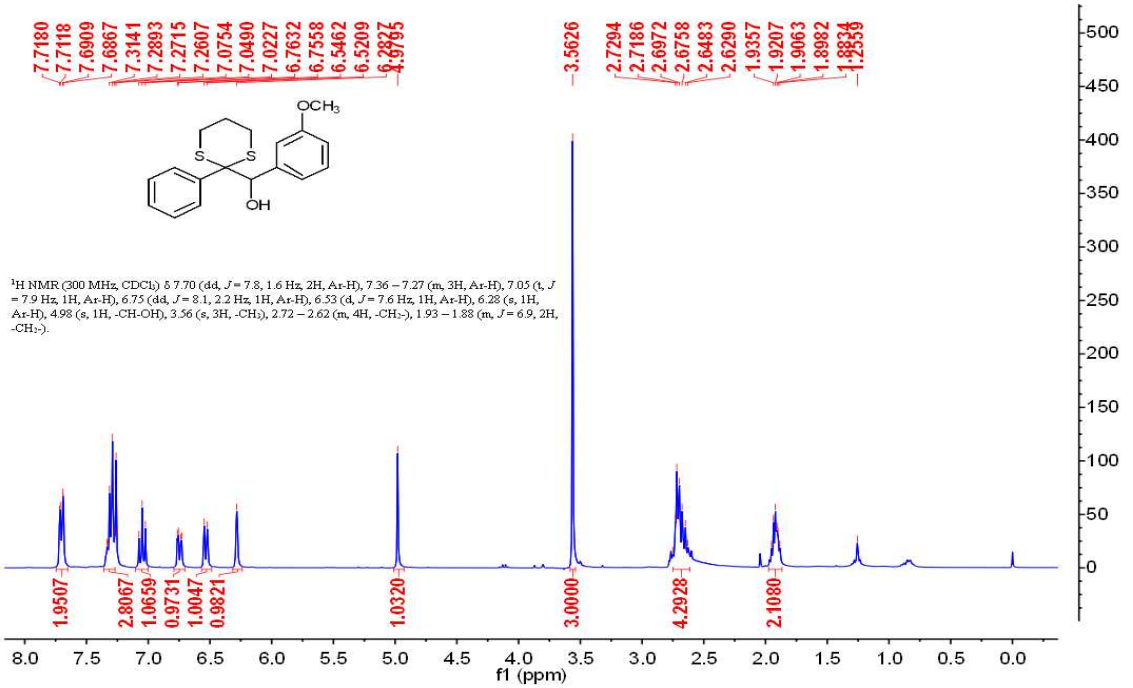


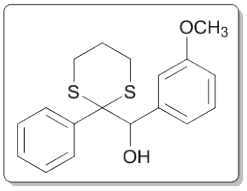
78% yield; colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (dd, J = 7.7, 1.2 Hz, 2H, Ar-H), 7.39 – 7.28 (m, 3H, Ar-H), 5.17 (s, 1H, -CH-), 3.16 – 2.99 (m, 2H, -CH_2-), 2.90 (dt, J = 14.2, 3.7 Hz, 2H, -CH_2-), 2.22 – 2.09 (m, 1H, -CH_2-), 2.01 – 1.83 (m, 1H, -CH_2-).



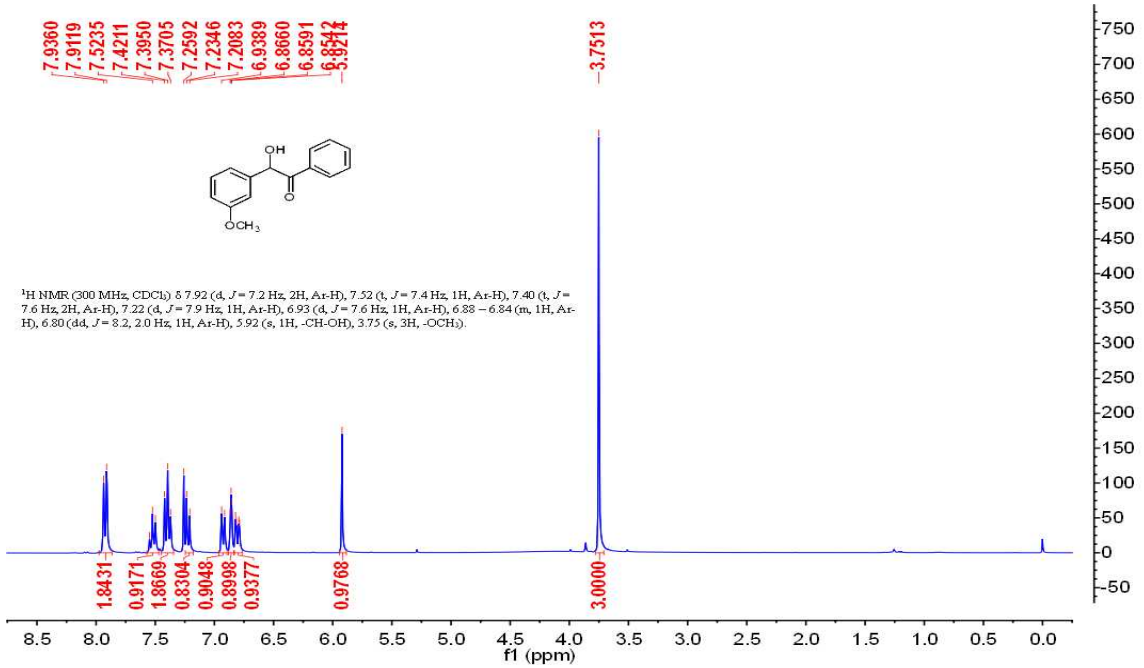


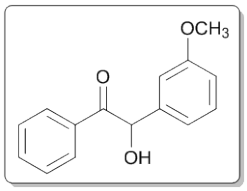
83% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.18 (dt, *J* = 14.5, 7.7 Hz, 5H, Ar-H), 6.90 (d, *J* = 7.2 Hz, 2H, Ar-H), 6.82 (dd, *J* = 8.0, 1.9 Hz, 1H, Ar-H), 4.95 (s, 1H, -CH-OH), 3.67 (s, 3H, -OCH_3), 2.70 (t, *J* = 11.6 Hz, 4H, -CH_2-), 2.04 (s, 1H, -OH), 1.92 (dd, *J* = 10.7, 6.5 Hz, 2H, -CH_2-).



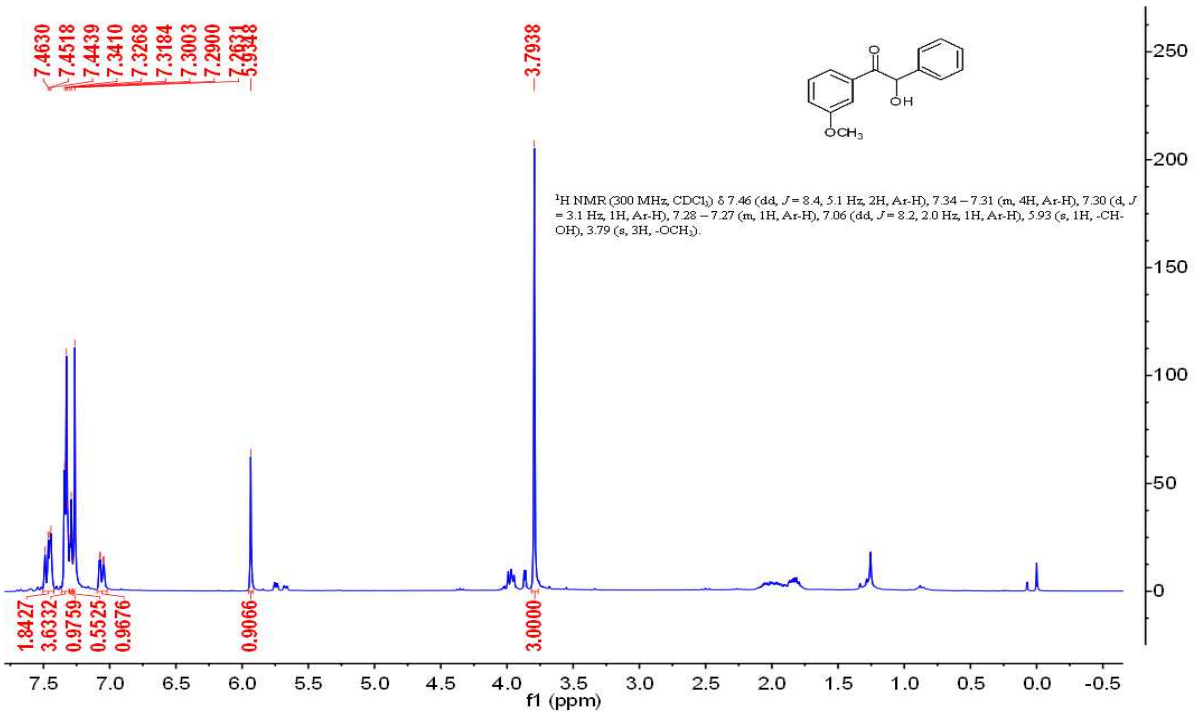


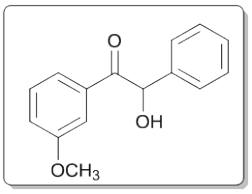
86% yield; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.8, 1.6 Hz, 2H, Ar-H), 7.36 – 7.27 (m, 3H, Ar-H), 7.05 (t, *J* = 7.9 Hz, 1H, Ar-H), 6.75 (dd, *J* = 8.1, 2.2 Hz, 1H, Ar-H), 6.53 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.28 (s, 1H, Ar-H), 4.98 (s, 1H, -CH-OH), 3.56 (s, 3H, $-CH_3$), 2.72 – 2.62 (m, 4H, $-CH_2$-), 1.93 – 1.88 (m, *J* = 6.9, 2H, $-CH_2$-).





88% yield; light yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.52 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.40 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.22 (d, *J* = 7.9 Hz, 1H, Ar-H), 6.93 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.88 – 6.84 (m, 1H, Ar-H), 6.80 (dd, *J* = 8.2, 2.0 Hz, 1H, Ar-H), 5.92 (s, 1H, -CH-OH), 3.75 (s, 3H, $-OCH_3$).





78% yield; light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ7.46 (dd, *J* = 8.4, 5.1 Hz, 2H, Ar-H), 7.34 – 7.31 (m, 4H, Ar-H), 7.30 (d, *J* = 3.1 Hz, 1H, Ar-H), 7.28 – 7.27 (m, 1H, Ar-H), 7.06 (dd, *J* = 8.2, 2.0 Hz, 1H, Ar-H), 5.93 (s, 1H, -CH-OH), 3.79 (s, 3H, -OCH_3).

5. The HPLC diagram of a mixture of $3e_2$, $4e_2$, $5e_2$, $6e_2$ and $7e_2$

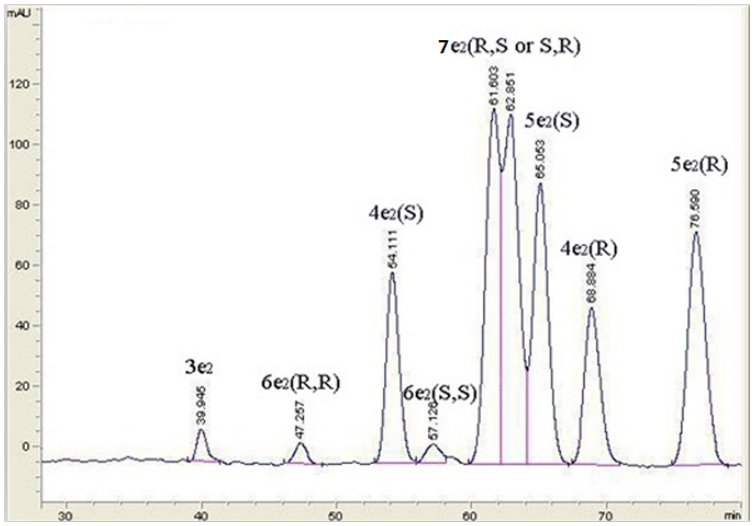


Fig.S1 The isolation of **$3e_2$**, **$4e_2$**, **$5e_2$**, **$6e_2$** and **$7e_2$** by using HPLC

A mixture of **$3e_2$** (t_R=39.945 min), **$4e_2$** [t_R=54.111 min (S) and 68.884 min (R)], **$5e_2$** [t_R=65.063 min (S) and 76.590 min (R)], **$6e_2$** [t_R=47.257 min (R, R) and 57.126 min (S, S)] and **$7e_2$** [t_R=61.603 min (R, S) and 62.851 min (S, R)] was completely isolated and identified by HPLC on a chiral stationary phase using an OJ-H column; eluent: *n*-hexane/*i*-PrOH (90:10); flow rate: 1.0 mL min^{-1}; UV detector: λ=220.

6. Dynamic kinetic study of $3e_2$

Table S1. The contents of intermediates and products during the catalytic reaction[a]

Entry	T(h)	**3e₂**(%)[b]	**4e₂**(%)[b]	**5e₂**(%)[b]	**6e₂**(%)[b]
1	0.5	56.747	16.049	23.477	3.728
2	1	19.215	26.997	36.376	13.685
3	1.5	4.04	29.836	36.741	29.383
4	2	0.994	26.144	29.534	43.328
5	2.5	1.194	23.731	27.662	47.413
6	3	2.362	11.447	12.712	73.478
7	6	0.710	4.772	6.616	87.9
8	9	0.319	4.53	7.453	87.697
9	12	0.231	2.43	3.579	93.76
10	15	0.309	1.239	2.224	96.228
11	18	0.142	1.018	1.59	97.251
12	21	0	0.43	0.995	98.575
13	24	0	0	0	100

[a] S/C=100:1, HCOOH:N(C_2H_5)$_3$ molar ratio = 2:1, none solvent, 40℃, **(R, R)-Ru a** as the catalyst.

[b] Determined by HPLC using an OJ-H column based on peak areas.

7. Dynamic kinetic study of $4e_2$

Table S2. The contents of intermediates and products during the catalytic reaction[a]

Entry	T(h)	**4e₂(S)**(%)[b]	**4e₂(R)**(%)[b]	**5e₂(S)**(%)[b]	**5e₂(R)**(%)[b]	**6e₂**(%)[b]
1	0	50	50	0	0	0
2	0.5	8.908	33.371	5.139	12.746	39.837
3	1	4.403	24.563	5.365	16.134	49.535
4	1.5	4.356	20.747	5.904	16.683	52.31
5	2	3.242	15.684	4.607	15.094	61.374
6	2.5	3.133	11.538	5.583	13.138	66.609
7	3	2.511	9.030	3.257	11.610	73.56
8	6	0.696	1.589	1.672	2.372	93.672
9	9	0	0	0	0	100

[a] S/C=100:1, HCOOH:N(C_2H_5)$_3$ molar ratio = 2:1, none solvent, 40℃, **(R,R)-Ru a** as a catalyst.

[b] Determined by HPLC using an OJ-H column based on peak areas.

8. Dynamic kinetic study of $5e_2$

Table S2. The contents of intermediates and products during the catalytic reaction[a]

Entry	T(h)	**4e₂(S)**(%)[b]	**4e₂(R)**(%)[b]	**5e₂(S)**(%)[b]	**5e₂(R)**(%)[b]	**6e₂**(%)[b]
1	0	0	0	50	50	0
2	1	1.766	7.623	4.422	40.418	45.771
3	2	2.389	8.643	4.304	28.890	55.773
4	3	1.722	6.653	3.129	15.172	73.323
5	4	1.437	4.374	2.534	8.374	83.281

6	5	0.895	2.924	1.757	4.856	89.568
7	6	0.534	1.335	1.413	2.273	94.446
8	9	0	0	0	0	100

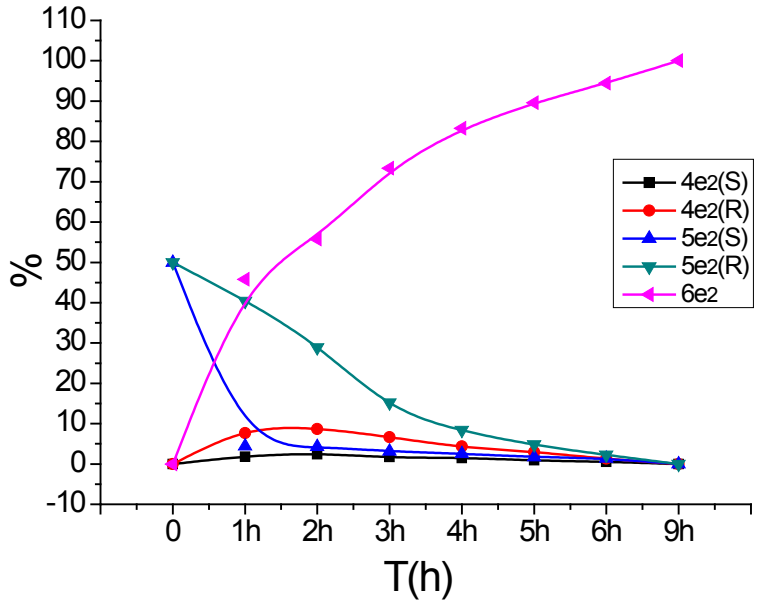
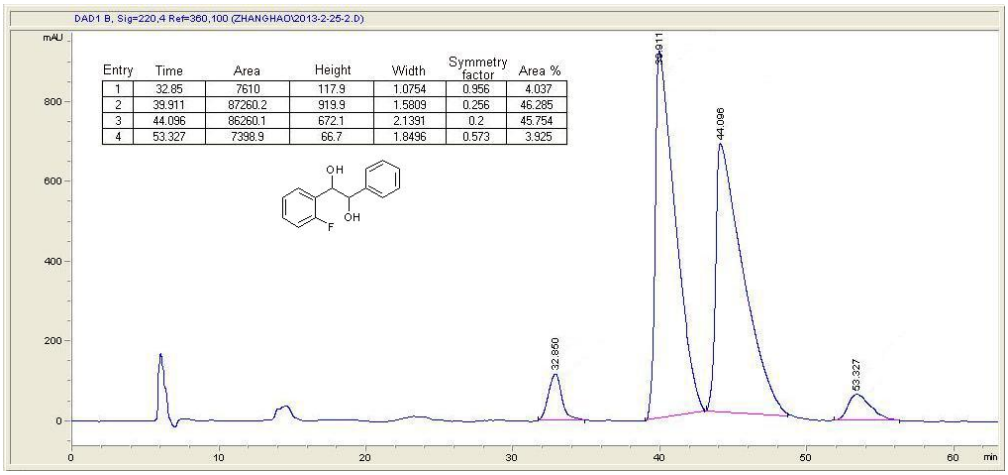
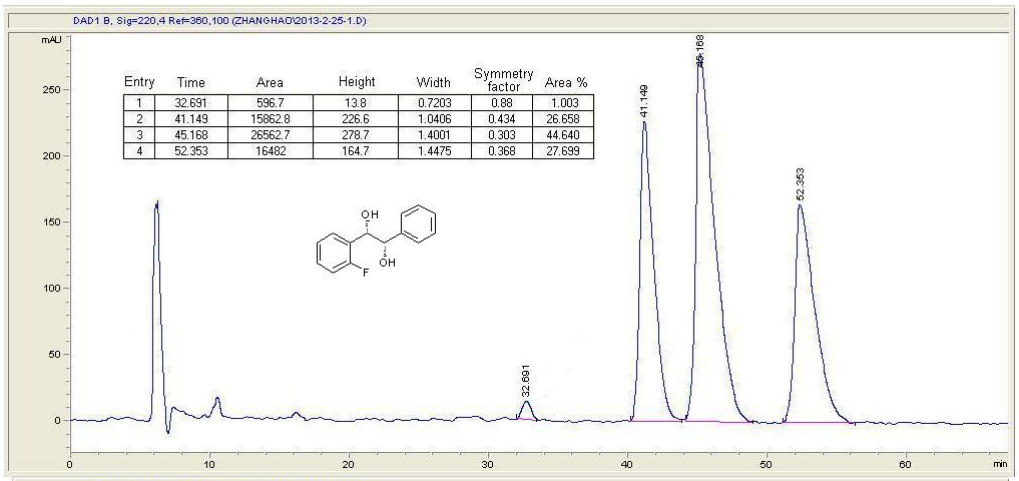


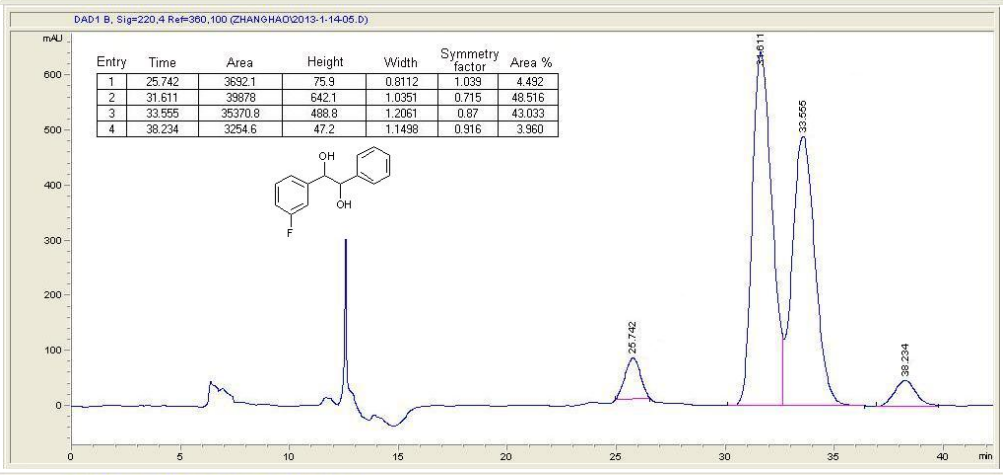
Fig.S2 The reactivity profiles of racemic α-hydroxy ketones **4e$_2$** plotted versus time within 9 h

9. HPLC spectra of products 6a-f

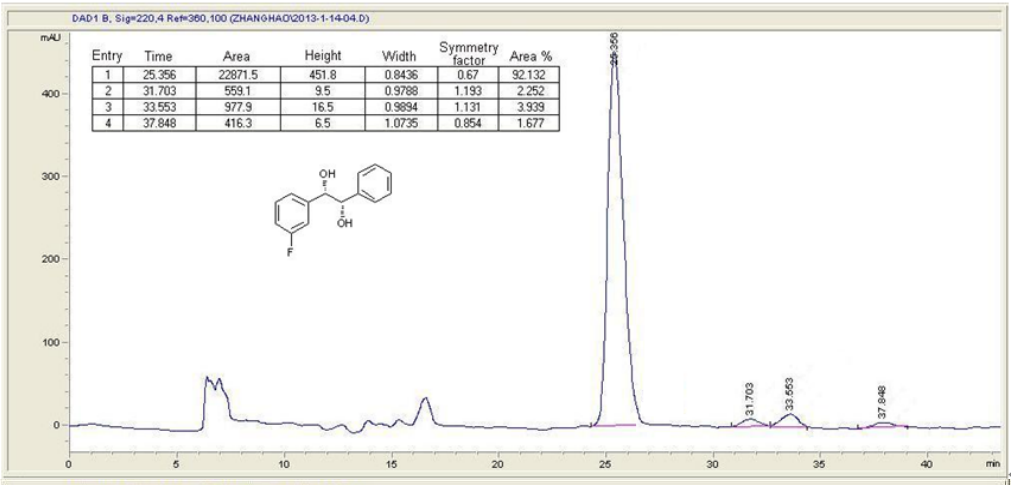




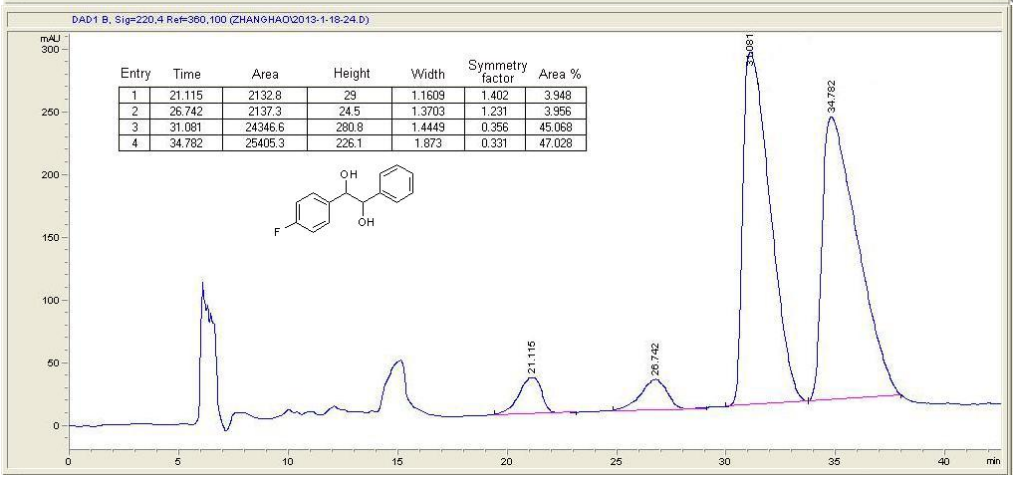
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	32.691	596.7	13.8	0.7203	0.88	1.003
2	41.149	15862.8	226.6	1.0406	0.434	26.658
3	45.168	26562.7	278.7	1.4001	0.303	44.640
4	52.353	16482	164.7	1.4475	0.368	27.699



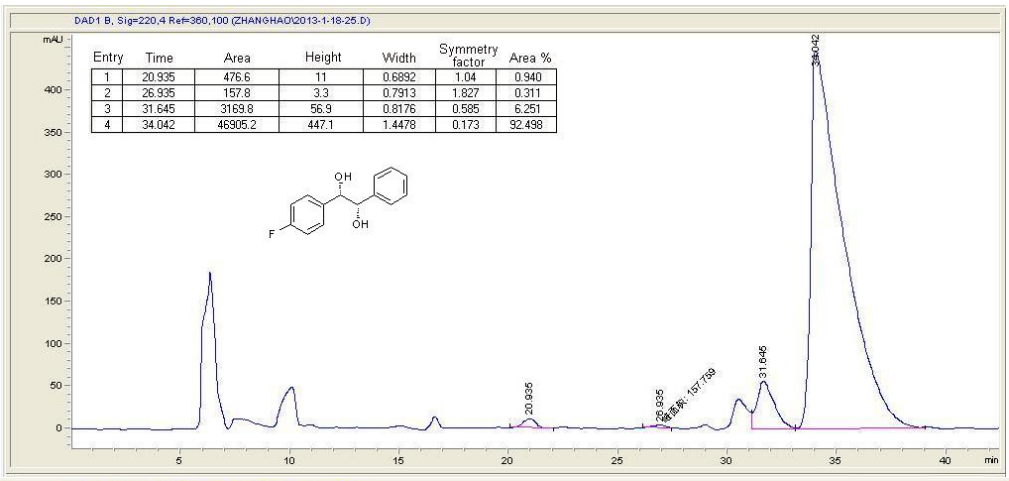
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	25.742	3692.1	75.9	0.8112	1.039	4.492
2	31.611	39878	642.1	1.0351	0.715	48.516
3	33.555	35370.8	488.8	1.2061	0.87	43.033
4	38.234	3254.6	47.2	1.1498	0.916	3.960



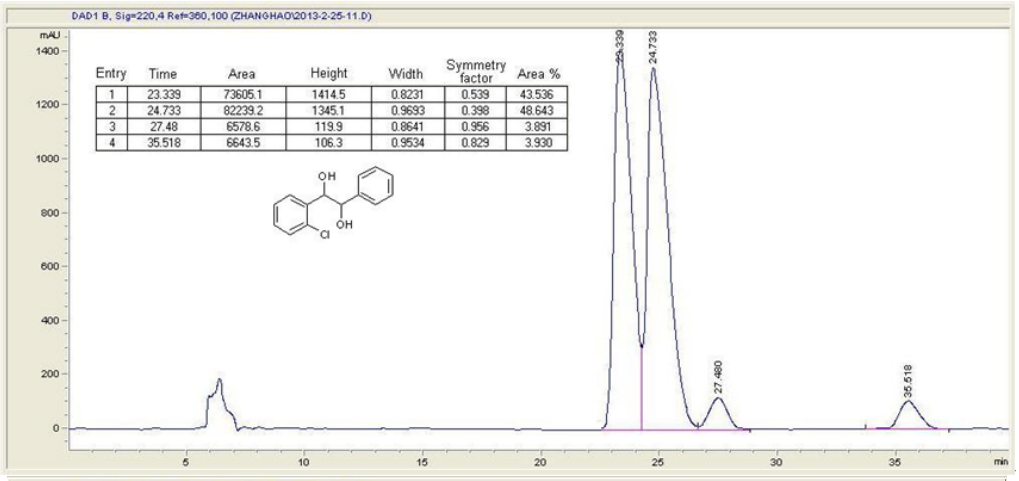
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	25.356	22871.5	451.8	0.8436	0.67	92.132
2	31.703	559.1	9.5	0.9788	1.193	2.252
3	33.553	977.9	16.5	0.9894	1.131	3.939
4	37.848	416.3	6.5	1.0735	0.854	1.677



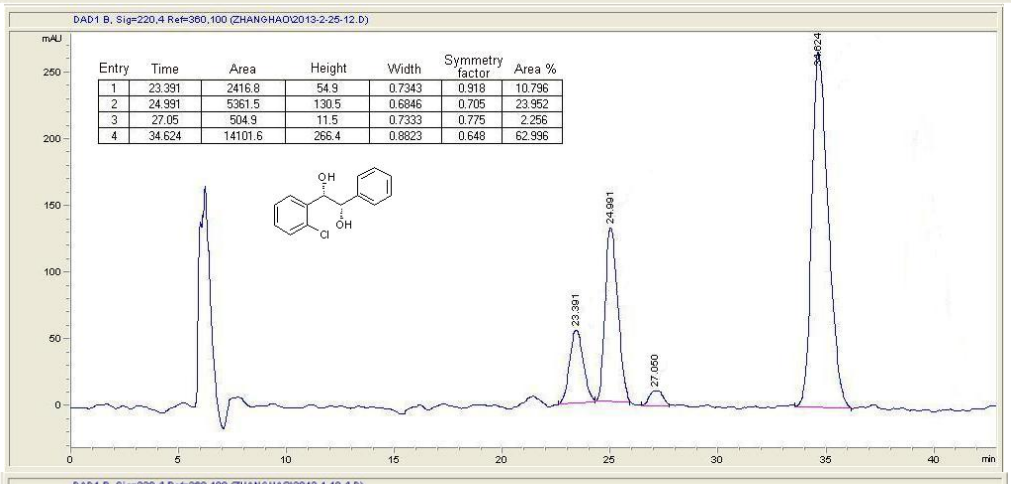
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	21.115	2132.8	29	1.1609	1.402	3.948
2	26.742	2137.3	24.5	1.3703	1.231	3.956
3	31.081	24346.6	280.8	1.4449	0.356	45.068
4	34.782	25405.3	226.1	1.873	0.331	47.028



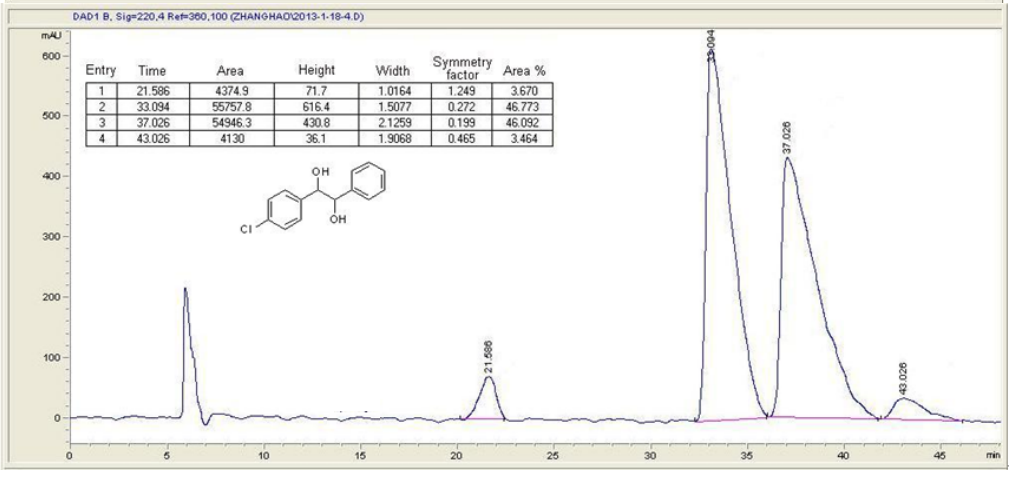
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	20.935	476.6	11	0.6892	1.04	0.940
2	26.935	157.8	3.3	0.7913	1.827	0.311
3	31.645	3169.8	56.9	0.8176	0.585	6.251
4	34.042	46905.2	447.1	1.4478	0.173	92.498



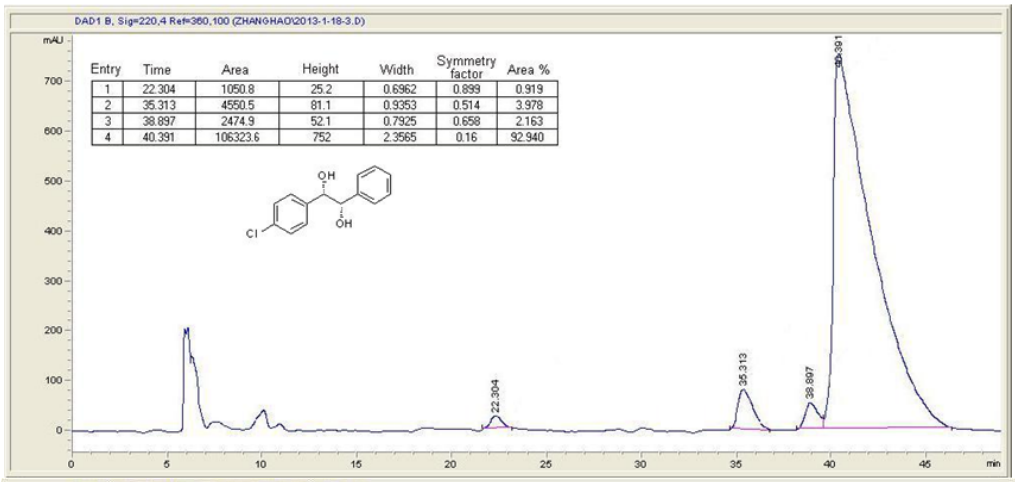
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	23.339	73605.1	1414.5	0.8231	0.539	43.536
2	24.733	82239.2	1345.1	0.9693	0.398	48.643
3	27.48	6578.6	119.9	0.8641	0.956	3.891
4	35.518	6643.5	106.3	0.9534	0.829	3.930



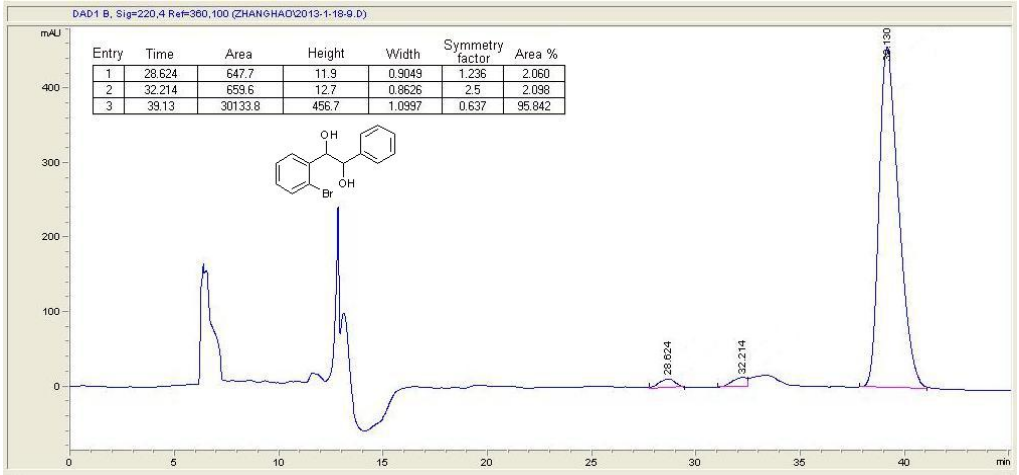
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	23.391	2416.8	54.9	0.7343	0.918	10.796
2	24.991	5361.5	130.5	0.6846	0.705	23.952
3	27.05	504.9	11.5	0.7333	0.775	2.256
4	34.624	14101.6	266.4	0.8823	0.648	62.996



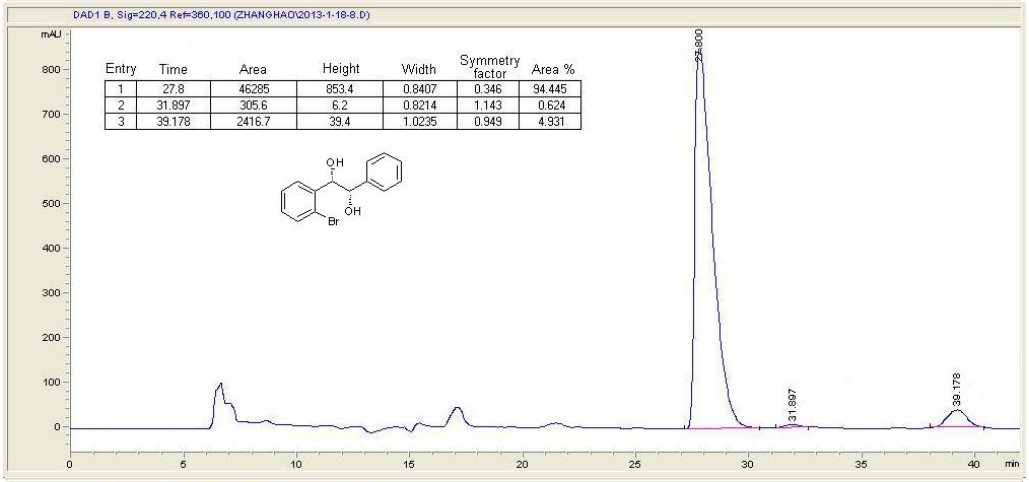
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	21.586	4374.9	71.7	1.0164	1.249	3.670
2	33.094	55757.8	616.4	1.5077	0.272	46.773
3	37.026	54946.3	430.8	2.1259	0.199	46.092
4	43.026	4130	36.1	1.9068	0.465	3.464



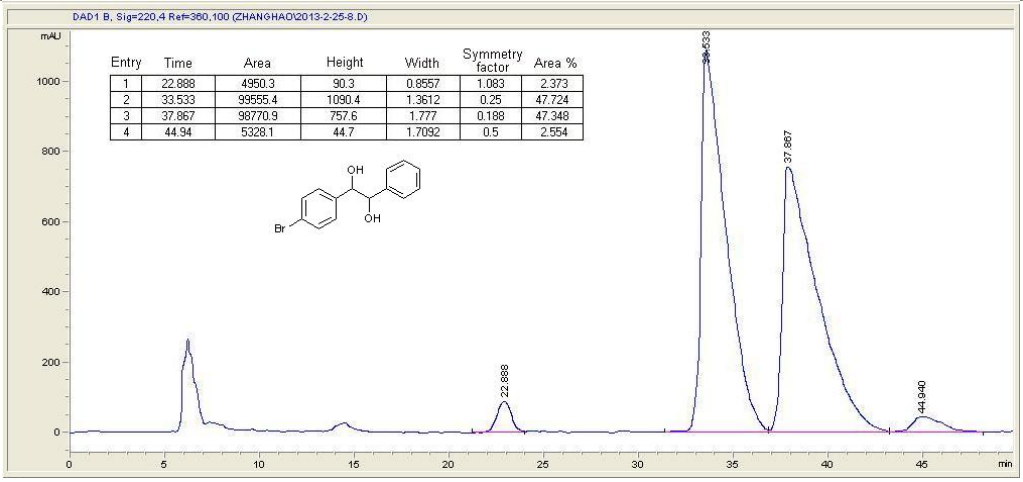
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	22.304	1050.8	25.2	0.6962	0.899	0.919
2	35.313	4550.5	81.1	0.9353	0.514	3.978
3	38.897	2474.9	52.1	0.7925	0.658	2.163
4	40.391	106323.6	752	2.3565	0.16	92.940



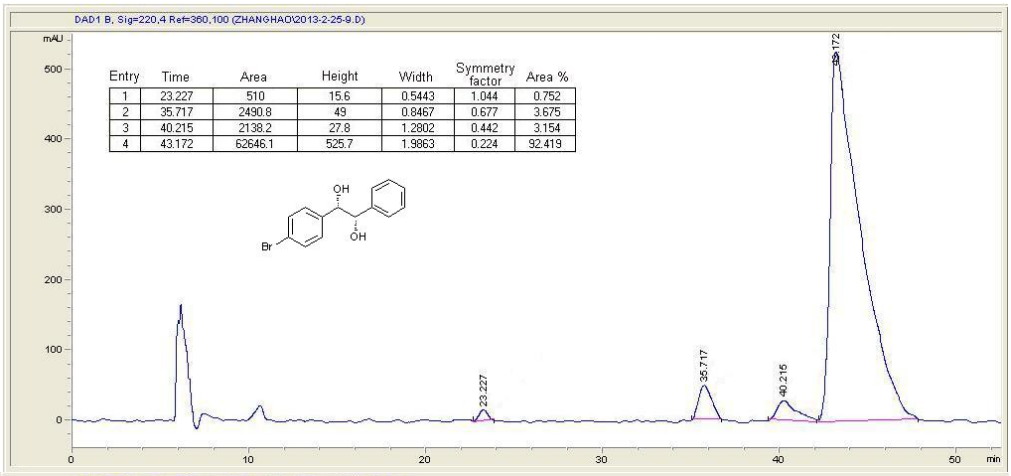
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	28.624	647.7	11.9	0.9049	1.236	2.060
2	32.214	659.6	12.7	0.8626	2.5	2.098
3	39.13	30133.8	456.7	1.0997	0.637	95.842



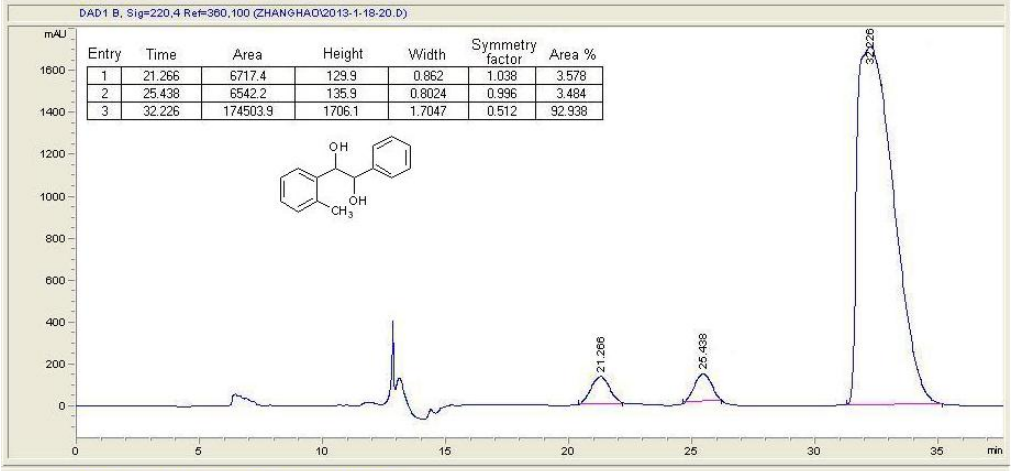
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	27.8	46285	853.4	0.8407	0.346	94.445
2	31.897	305.6	6.2	0.8214	1.143	0.624
3	39.178	2416.7	39.4	1.0235	0.949	4.931



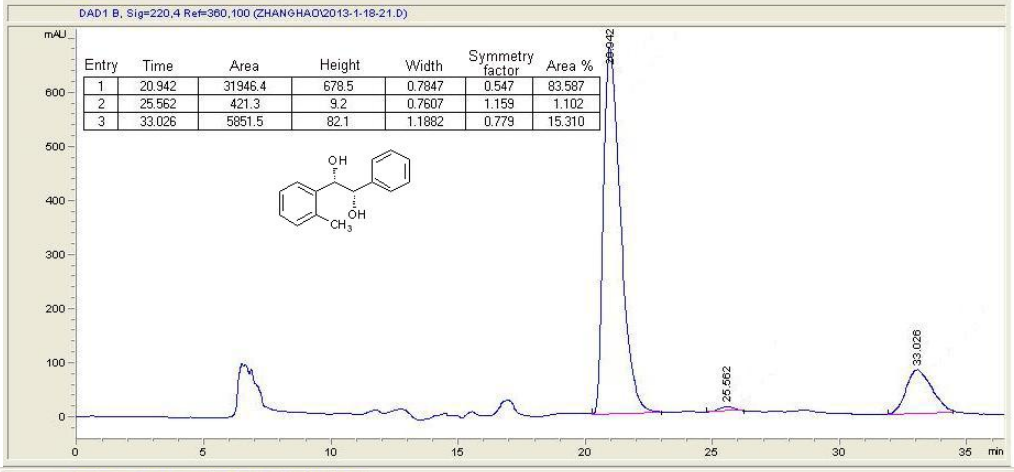
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	22.888	4950.3	90.3	0.8557	1.083	2.373
2	33.533	99555.4	1090.4	1.3612	0.25	47.724
3	37.867	98770.9	757.6	1.777	0.188	47.348
4	44.94	5328.1	44.7	1.7092	0.5	2.554



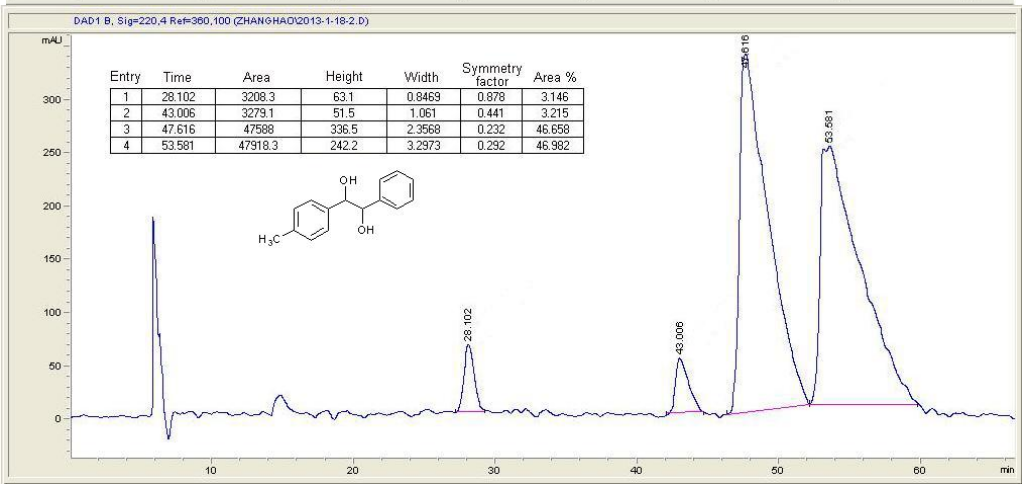
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	23.227	510	15.6	0.5443	1.044	0.752
2	35.717	2490.8	49	0.8467	0.677	3.675
3	40.215	2138.2	27.8	1.2802	0.442	3.154
4	43.172	62646.1	525.7	1.9863	0.224	92.419



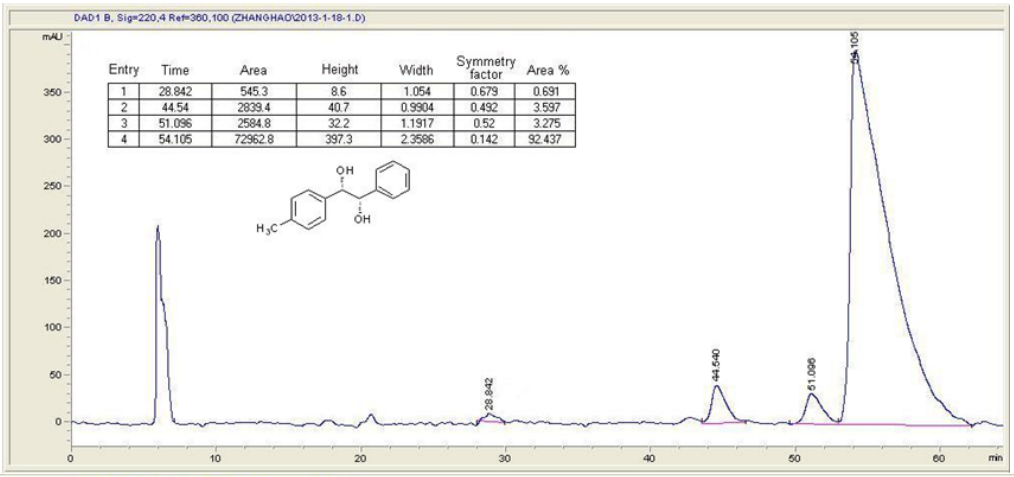
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	21.266	6717.4	129.9	0.862	1.038	3.578
2	25.438	6542.2	135.9	0.8024	0.996	3.484
3	32.226	174503.9	1706.1	1.7047	0.512	92.938



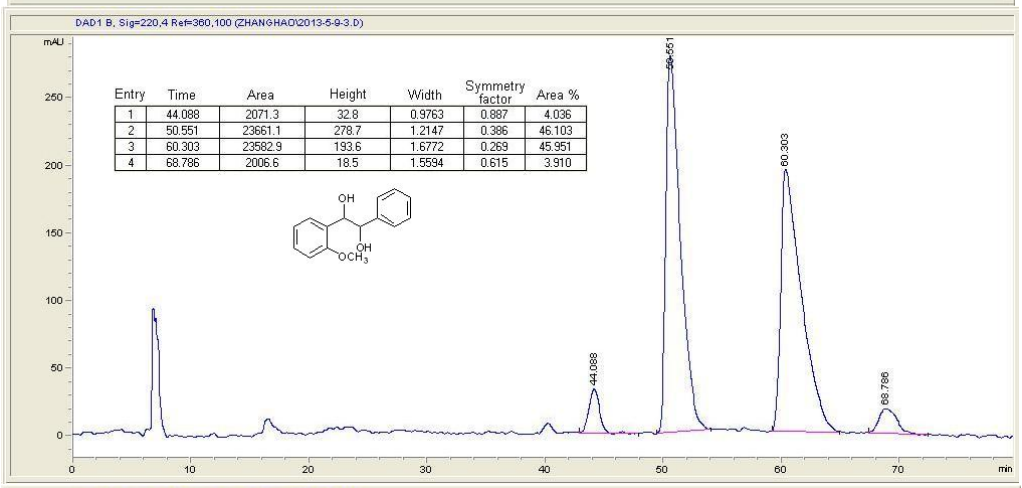
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	20.942	31946.4	678.5	0.7847	0.547	83.587
2	25.562	421.3	9.2	0.7607	1.159	1.102
3	33.026	5851.5	82.1	1.1882	0.779	15.310



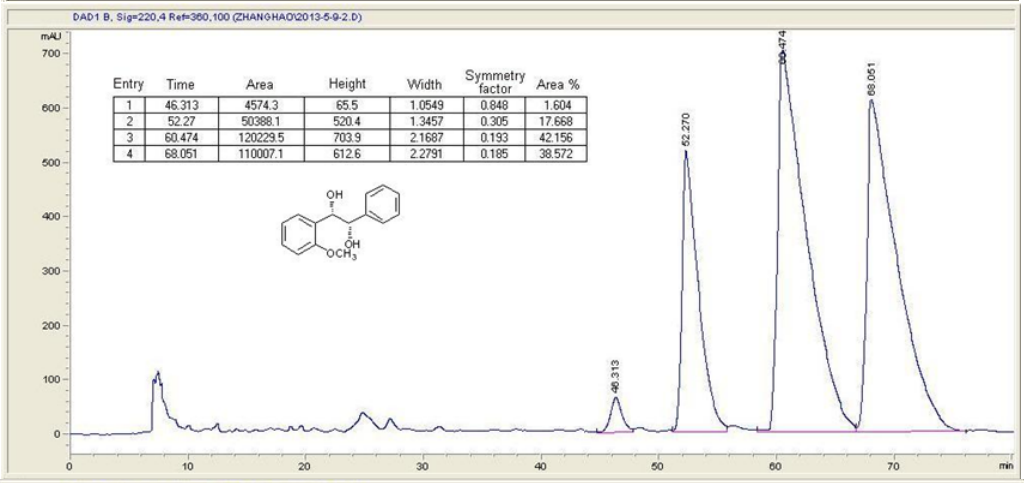
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	28.102	3208.3	63.1	0.8469	0.878	3.146
2	43.006	3279.1	51.5	1.061	0.441	3.215
3	47.616	47588	336.5	2.3568	0.232	46.658
4	53.581	47918.3	242.2	3.2973	0.292	46.982



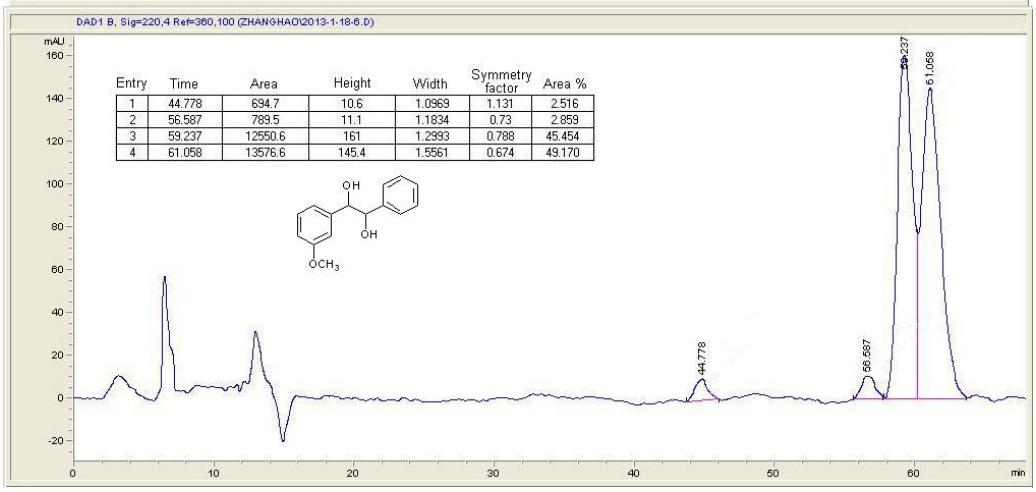
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	28.842	545.3	8.6	1.054	0.679	0.691
2	44.54	2839.4	40.7	0.9904	0.492	3.597
3	51.096	2584.8	32.2	1.1917	0.52	3.275
4	54.105	72962.8	397.3	2.3586	0.142	92.437



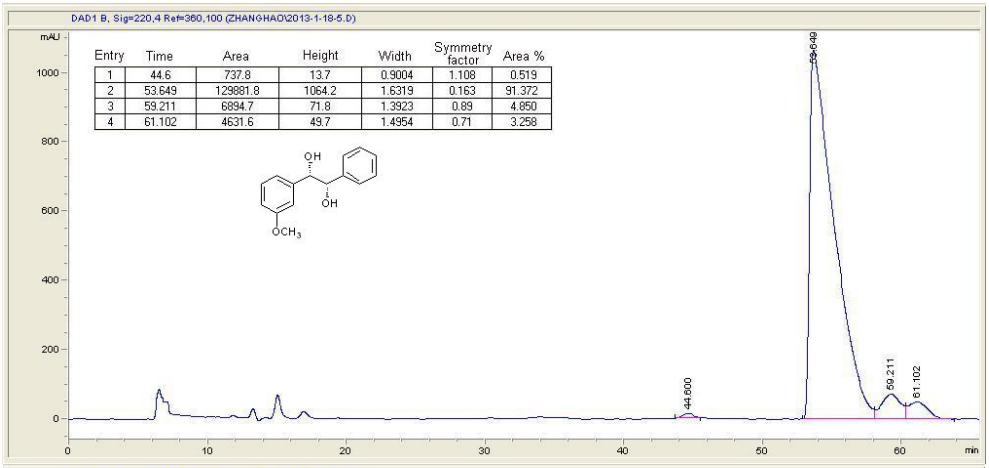
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	44.088	2071.3	32.8	0.9763	0.887	4.036
2	50.551	23661.1	278.7	1.2147	0.386	46.103
3	60.303	23582.9	193.6	1.6772	0.269	45.951
4	68.786	2006.6	18.5	1.5594	0.615	3.910



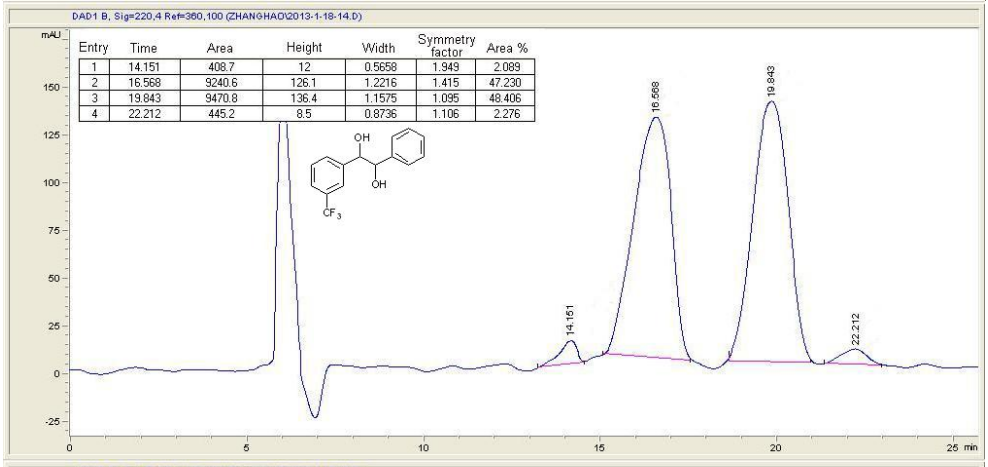
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	46.313	4574.3	65.5	1.0549	0.848	1.604
2	52.27	50388.1	520.4	1.3457	0.305	17.668
3	60.474	120229.5	703.9	2.1687	0.193	42.156
4	68.051	110007.1	612.6	2.2791	0.185	38.572



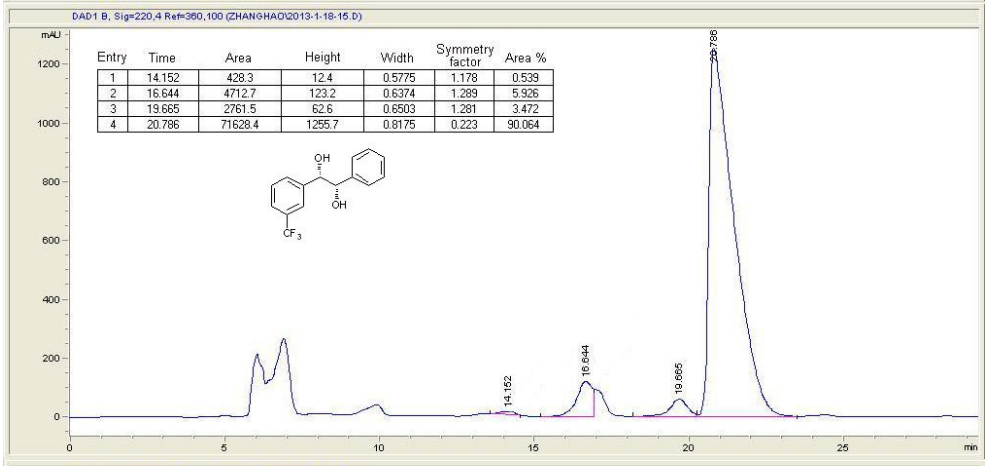
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	44.778	694.7	10.6	1.0969	1.131	2.516
2	56.587	789.5	11.1	1.1834	0.73	2.859
3	59.237	12550.6	161	1.2993	0.788	45.454
4	61.058	13576.6	145.4	1.5561	0.674	49.170



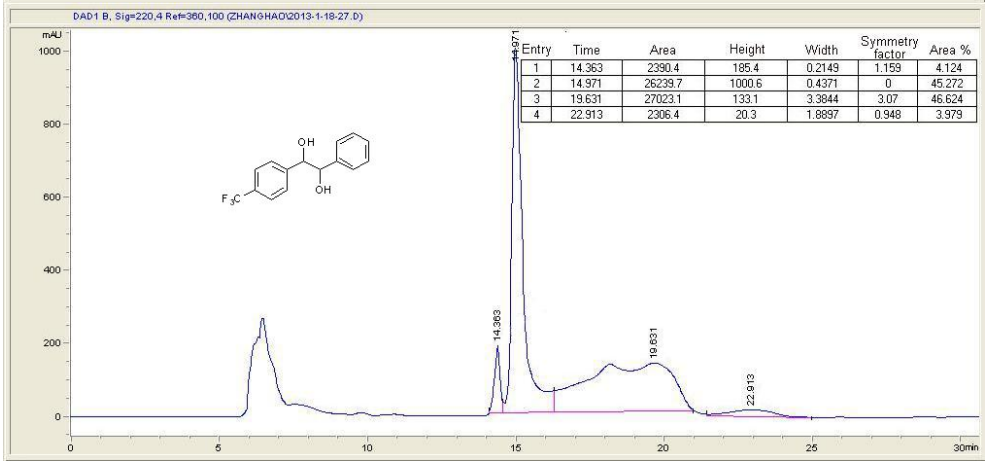
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	44.6	737.8	13.7	0.9004	1.108	0.519
2	53.649	129881.8	1064.2	1.6319	0.163	91.372
3	59.211	6894.7	71.8	1.3923	0.89	4.850
4	61.102	4631.6	49.7	1.4954	0.71	3.258



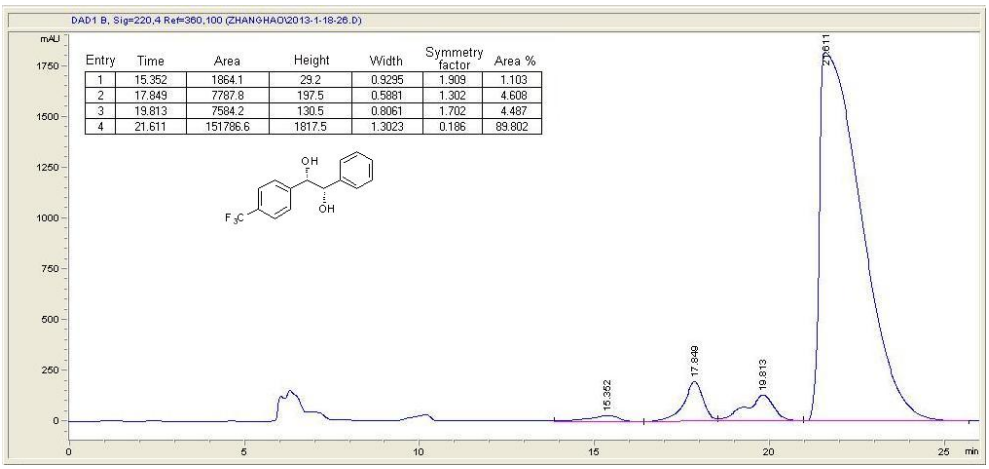
Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	14.151	408.7	12	0.5658	1.949	2.089
2	16.568	9240.6	126.1	1.2216	1.415	47.230
3	19.843	9470.8	136.4	1.1575	1.095	48.406
4	22.212	445.2	8.5	0.8736	1.106	2.276



Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	14.152	428.3	12.4	0.5775	1.178	0.539
2	16.644	4712.7	123.2	0.6374	1.289	5.926
3	19.665	2761.5	62.6	0.6503	1.281	3.472
4	20.786	71628.4	1255.7	0.8175	0.223	90.064



Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	14.363	2390.4	185.4	0.2149	1.159	4.124
2	14.971	26239.7	1000.6	0.4371	0	45.272
3	19.631	27023.1	133.1	3.3844	3.07	46.624
4	22.913	2306.4	20.3	1.8897	0.948	3.979



Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	15.352	1864.1	29.2	0.9295	1.909	1.103
2	17.849	7787.8	197.5	0.5881	1.302	4.608
3	19.813	7584.2	130.5	0.8061	1.702	4.487
4	21.611	151786.6	1817.5	1.3023	0.186	89.802