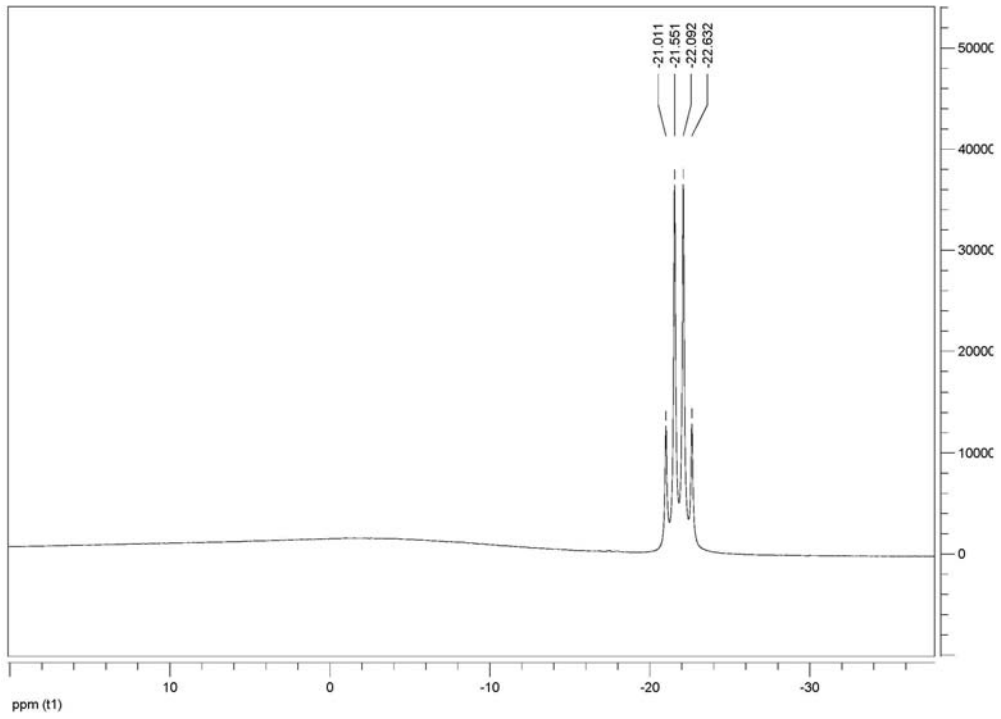
Electronic Supplementary Material (ESI) for RSC Advances

Calcium amidoborane, a new reagent for chemoselective reduction of α,β-unsaturated aldehydes and ketones to allylic alcohols

Weiliang Xu, Ruimin Wang, Guotao Wu and Ping Chen*

pchen@dicp.ac.cn

S1. ^{11}B NMR spectrum for synthesized CaAB



S2. Synthesis of α,β-unsaturated ketones (entry 11-15, entry 17-18, Table 1)

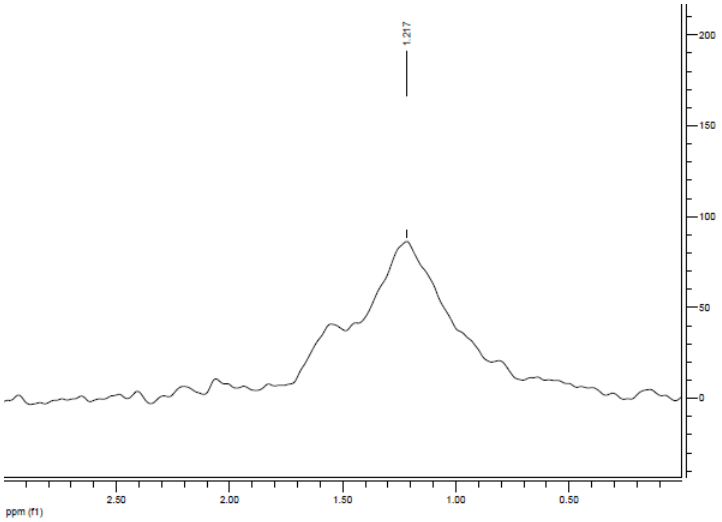
In a 50 mL flask, corresponding aldehyde (10 mmol), corresponding ketone (10 mmol) and ethanol (20 ml) were placed, and the solution was stirred at room temperature. To the solution, NaOH aqueous solution (1.5M, 10ml) was slowly added. After 5 hrs, the reaction mixture was neutralized with 2M aqueous HCl solution. Crude α,β-unsaturated ketone was obtained after filtration. Then, the crude product was recrystallized from ethanol.

S3. Synthesis of α,β-unsaturated ketones (entry 10, entry 19)

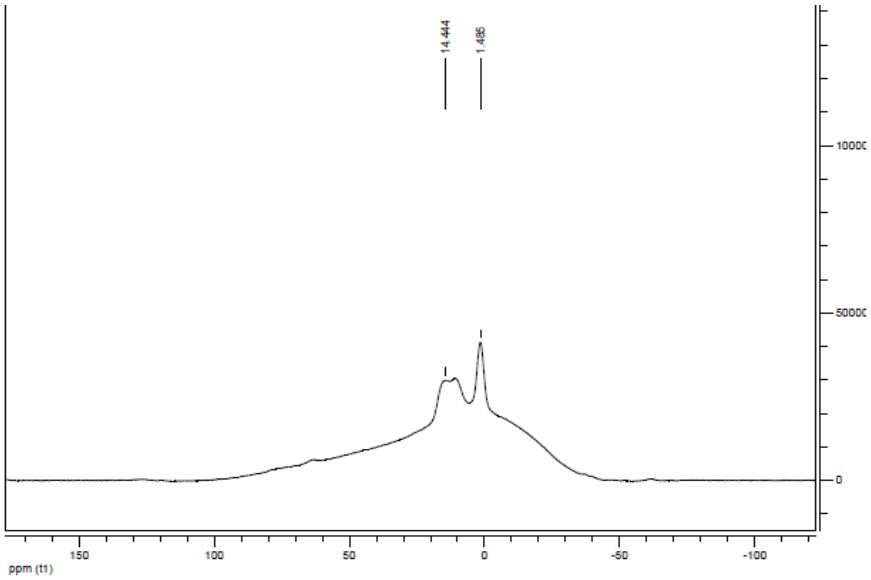
In a 50 mL flask, corresponding aldehyde (10 mmol), corresponding ketone (10 mmol) and ethanol (20 ml) were placed, and the solution was stirred at room temperature. To the solution, NaOH aqueous solution (1.5M, 10ml) was added slowly. After 5 hrs, the

reaction mixture was neutralized with 2M aqueous HCl solution. The solution was extracted with DCM (3 X 10 mL). The organic layer was washed with aqueous NaCl (2 X 10 mL) and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography with hexane/EtOAc (v/v,10/1) as an eluent to obtain α,β-unsaturated ketone.

S4. ^{2}H NMR result for $Ca(ND_2BH_3)_2$ (CaA(D)B) reacting cinnamaldehyde in THF



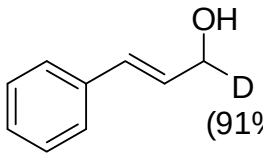
S5. ^{11}B MAS NMR spectrum for the precipitant from the reaction of LiAB and cinnamaldehyde



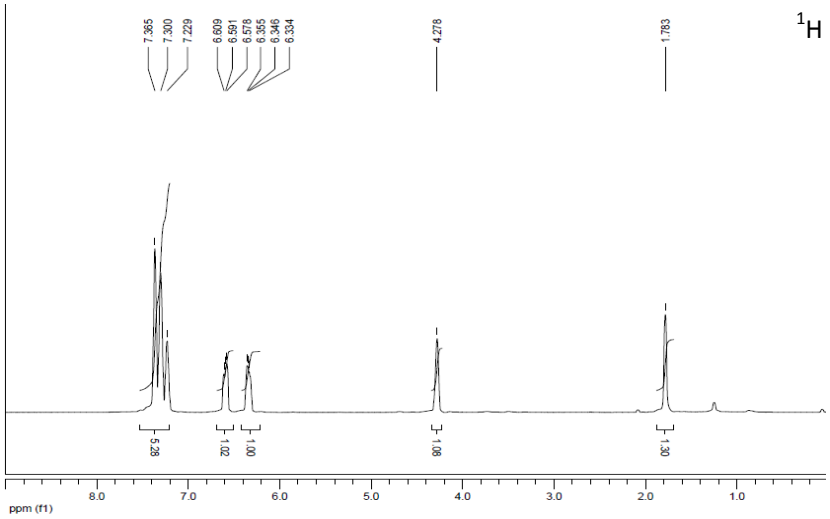
14 ppm is attributed to C_6H_5-C=C-CH_2O-BH=NH(Li);

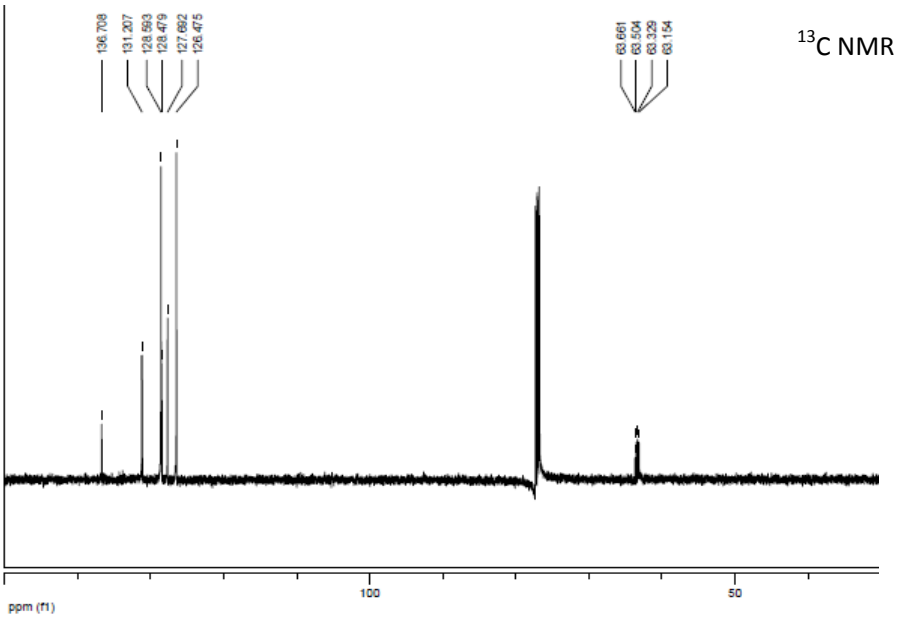
1.4ppm is attributed to $(C_6H_5\text{-}C{=}C\text{-}CH_2O)_2\text{-}B{=}NH(Li)$, which is the product of $C_6H_5\text{-}C{=}C\text{-}CH_2O\text{-}BH{=}NH(Li)$ reacting with another molecular of cinnamaldehyde.

S6. Characterization data for the isolated product after $LiNH_2BD_3$ (LiAB(D)) reacting with chalcone

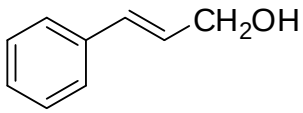


(91%) ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 1.78. (s, 1H; OH), 4.28 (s, 1H; CHD), 6.33-6.35 (m, 1H; CH), 6.57-6.60 (m, 1H; CH), 7.23-7.36 ppm (m, 5H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 63.38 (t, J_{CD}= 22.08 Hz; CD), 126.47, 127.69, 128.48, 128.54, 131.21, 136.71 ppm ; FT-IR (film): ν_{max} = 3348, 3081, 3058, 3027, 2147 (CD), 1494, 1448, 976 cm^{-1}; MS (EI): m/z (%) 135 $[M]^+$ (75), 92 (100), 78 (70), 106 (50).

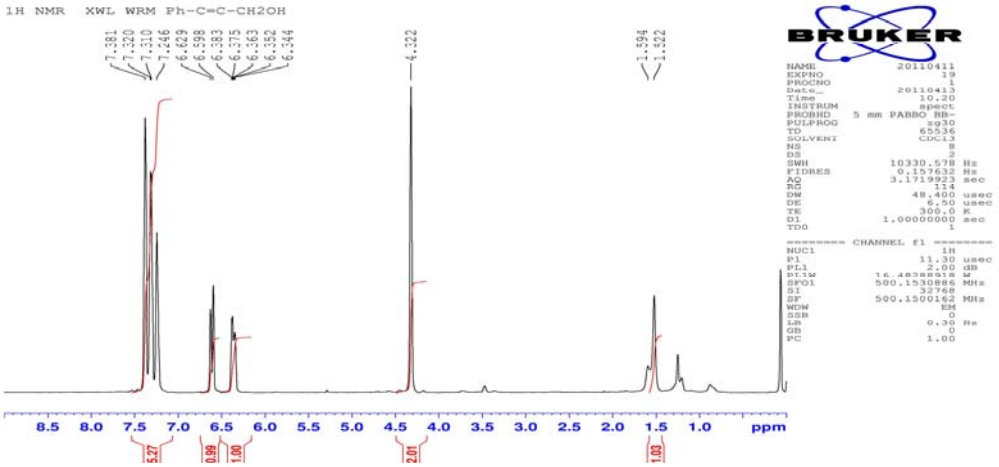


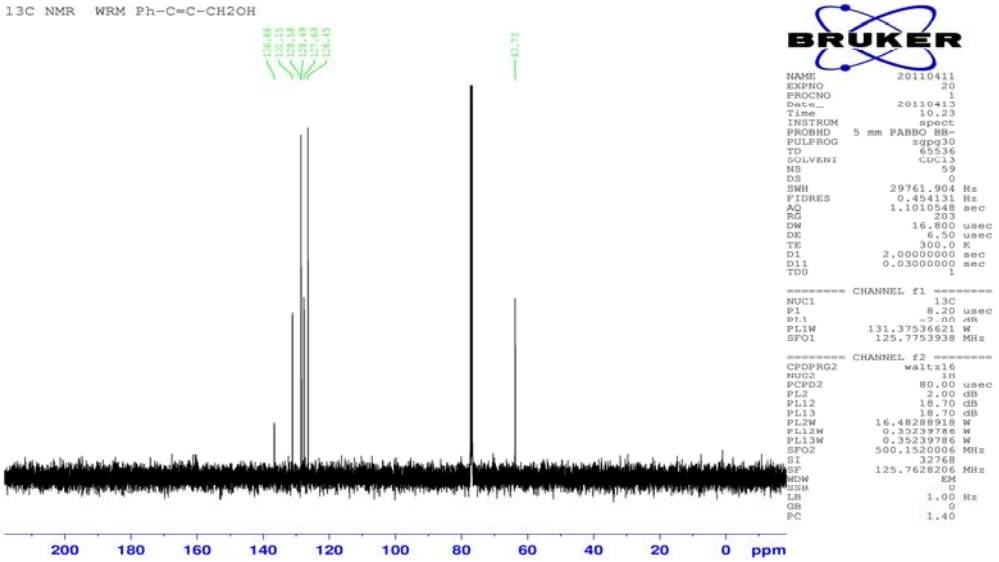


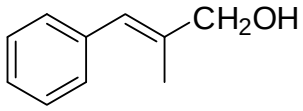
S6. Products characterizations and ^{1}H, ^{13}C NMR spectra.



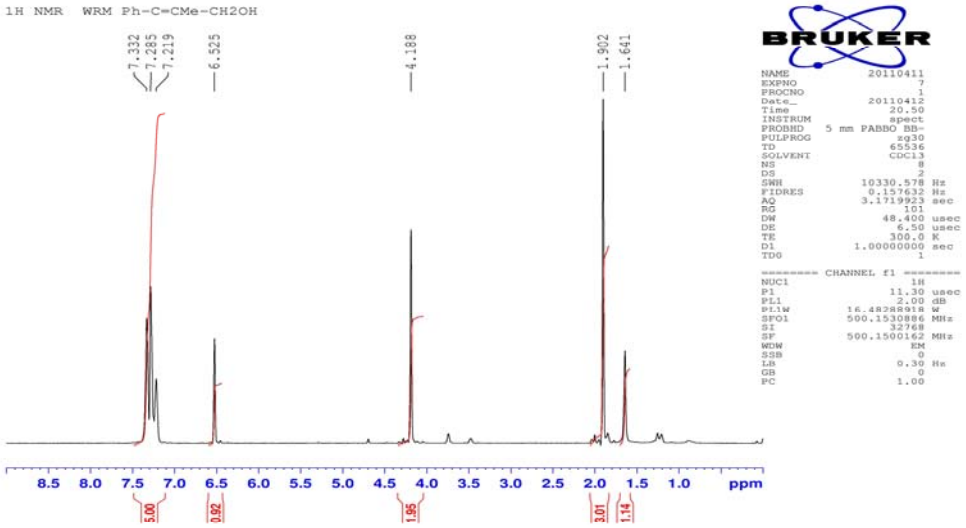
(entry 1, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 1.52. (s, 1H; OH), 4.33 (s, 2H; CH_2), 6.34-6.38 (m, 1H; CH), 6.61 (d, J_{HH}= 15.63 Hz,1H; CH), 7.24-7.38 ppm (m, 5H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 63.73, 126.45, 127.69, 128.48, 128.58, 131.21, 136.71 ppm ; FT-IR (film): ν_{max} = 3322, 3081, 3058, 3027, 2920, 2861, 1494, 1448, 966 cm^{-1}; MS (EI): m/z (%) 134 $[M]^{+}$ (50), 91 (100), 78 (60), 105 (40).

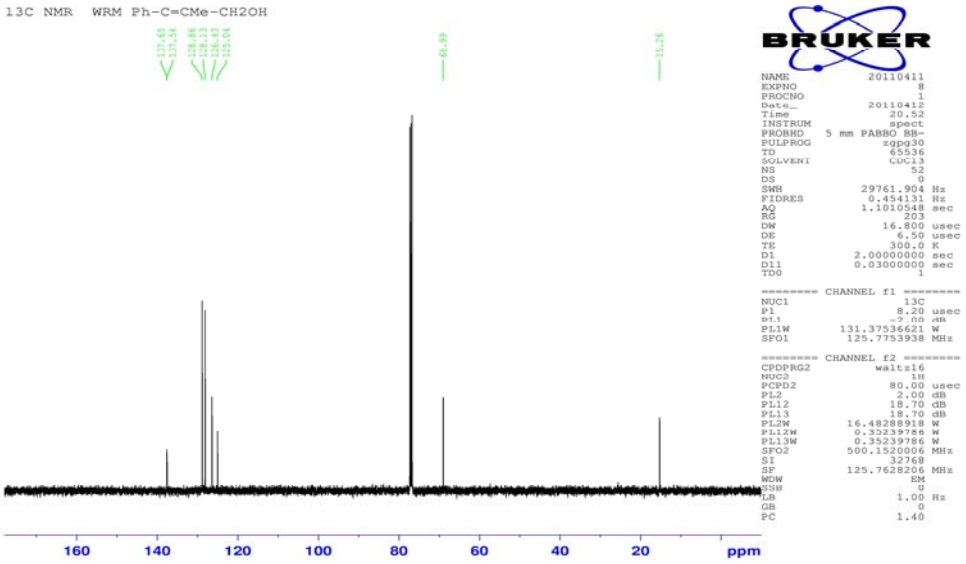


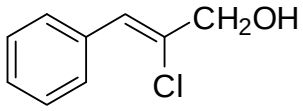




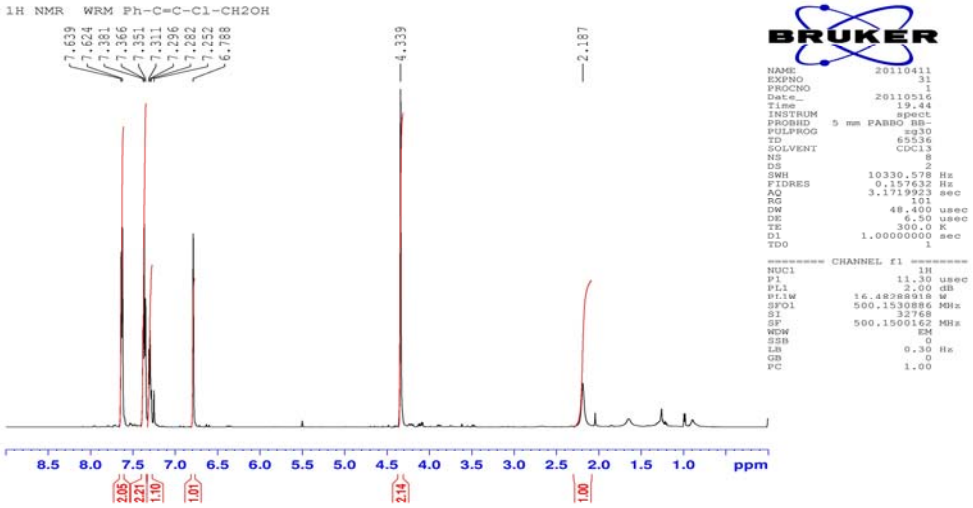
(entry 2, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 1.64. (s, 1H; OH), 1.90 (s, 3H; CH_3), 4.18 (s, 2H; CH_2), 6.52 (s, 1H; CH), 7.22-7.33 (m, 5H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 15.26, 68.99, 125.04, 126.43, 128.13, 128.86, 137.54, 137.65 ppm; FT-IR (film): ν_{max} = 3325, 3054, 3023, 2914, 2858, 1491, 1444, 1009 cm^{-1}; MS (EI): m/z (%) 148 $[M]^{+}$ (55), 91 (100), 115 (70), 105 (40).

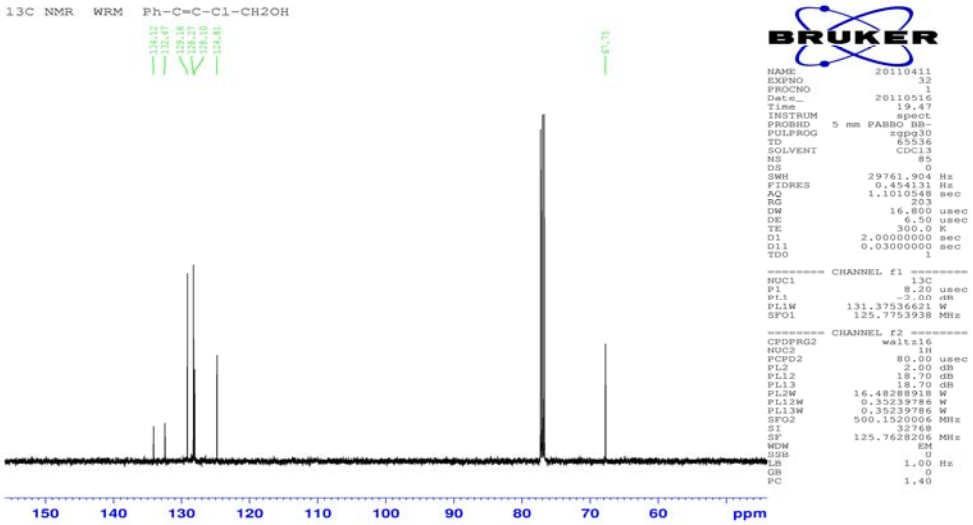


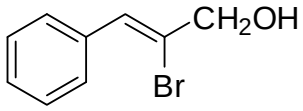




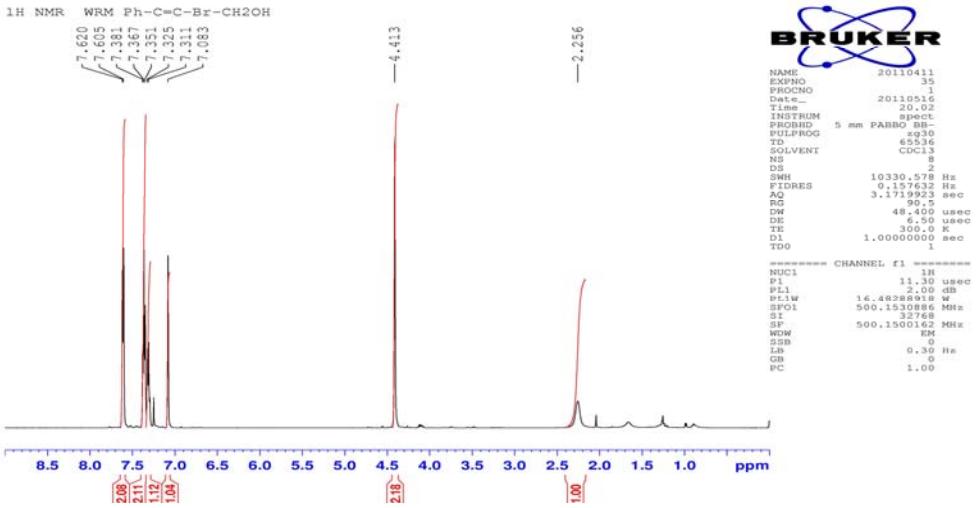
(entry 3, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 2.18. (s, 1H; OH), 4.34 (s, 2H; CH_2), 6.79 (s, 1H; CH), 7.25-7.64 (m, 5H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 67.75, 124.81, 128.10, 128.27, 129.16, 132.47, 134.12 ppm; FT-IR (film): ν_{max} = 3344, 3056, 3026, 2921, 2863, 1652, 1492, 1446 cm^{-1}; MS (EI): m/z (%) 168 $[M]^{+}$ (65), 115 (100), 133 (90), 102 (50).

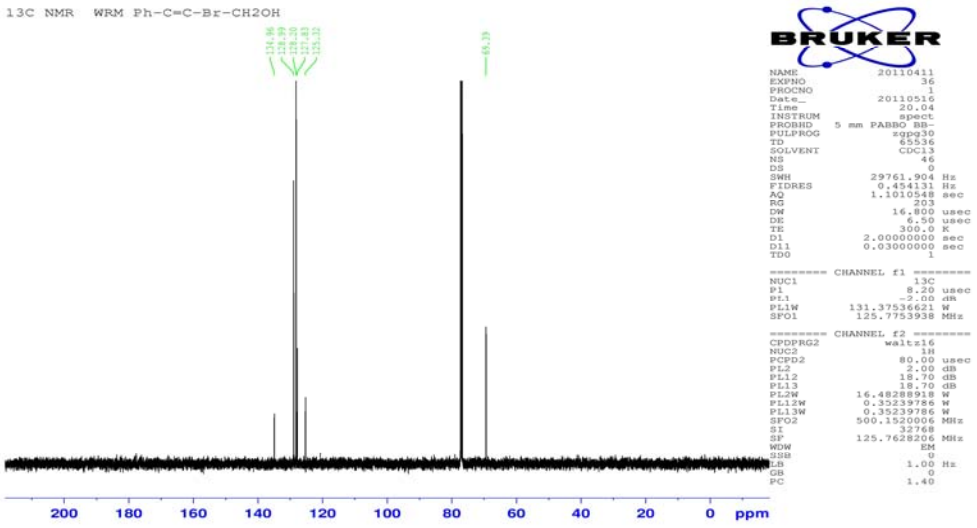


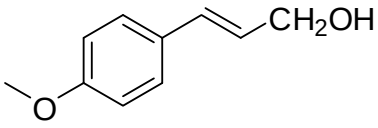




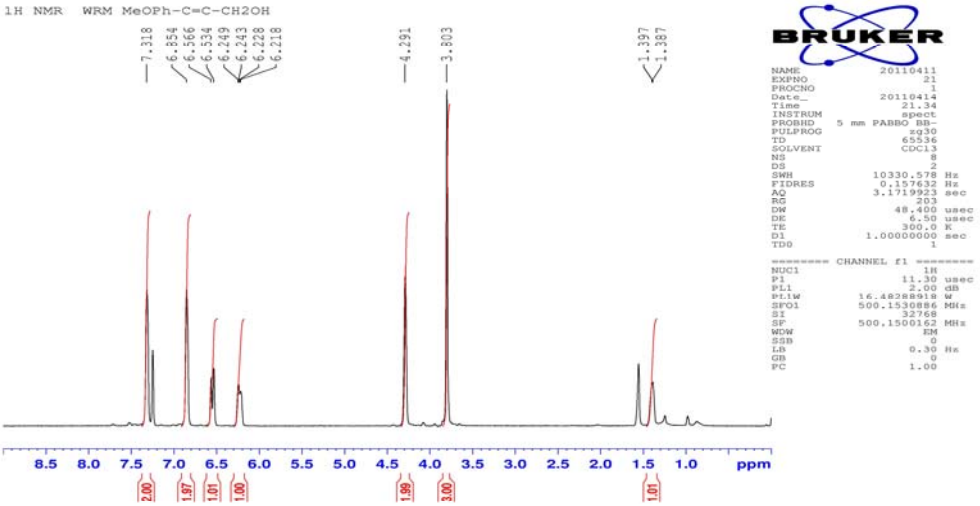
(entry 4, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 2.26 (s, 1H; OH), 4.41 (s, 2H; CH_2), 7.08 (s, 1H; CH), 7.31-7.62 (m, 5H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 69.39, 125.32, 127.83, 128.20, 128.99, 134.96 ppm; FT-IR (film): ν_{max} = 3338, 3056, 3025, 2918, 2858, 1646, 1491, 1445 cm^{-1}; MS (EI): m/z (%) 212 $[M-H]^{+}$ (50), 115 (100), 133 (90), 102 (50), 77 (55).

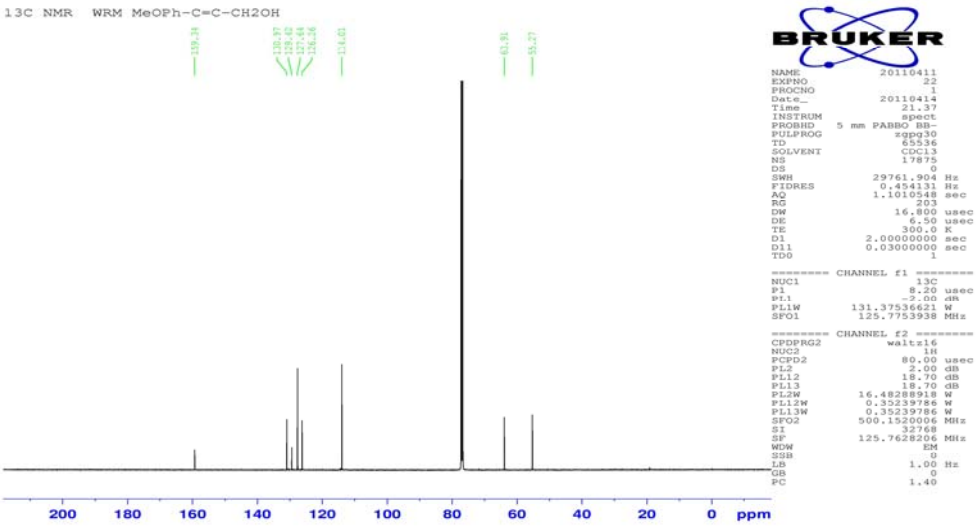


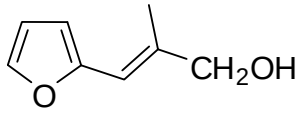




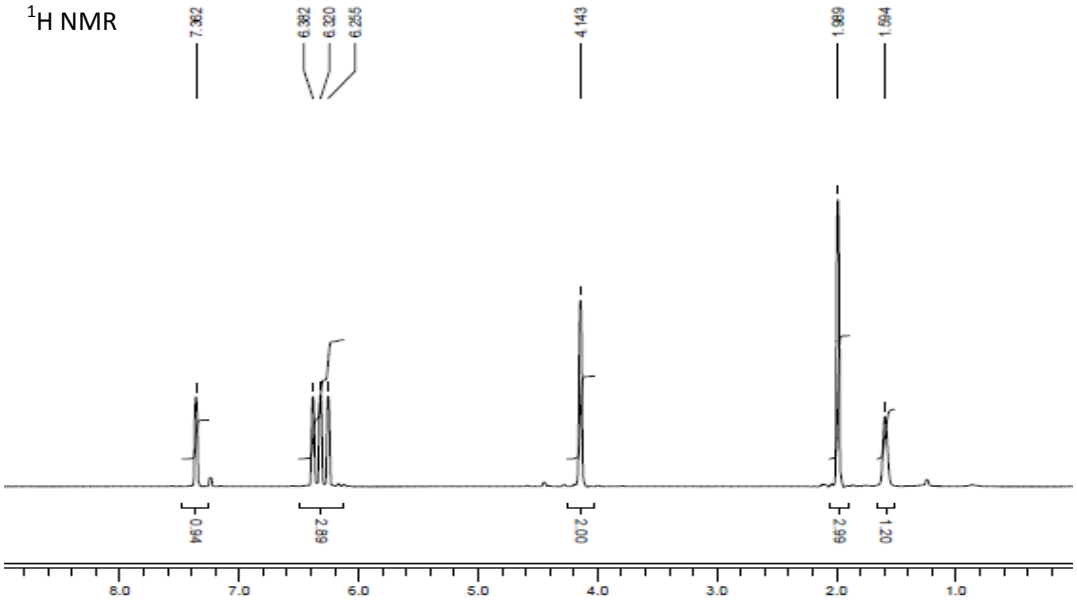
(entry 5, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 1.38 (s, 1H; OH), 3.80 (s, 3H; CH_3), 4.29 (s, 2H; CH_2), 6.21-6.24 (m, 1H; CH), 6.55 (d, J_{HH}= 15.87 Hz,1H; CH), 7.85-7.31 (m, 5H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ =55.27, 63.91, 114.01, 126.26, 127.64, 129.42, 130.97, 159.34 ppm; FT-IR (film): v_{max} = 3368, 3033, 2969, 2917, 2841, 1605, 1511, 1460 cm^{-1}; MS (EI): m/z (%) 164 $[M]^{+}$ (30), 121 (100), 108 (30), 77 (20), 91 (20).

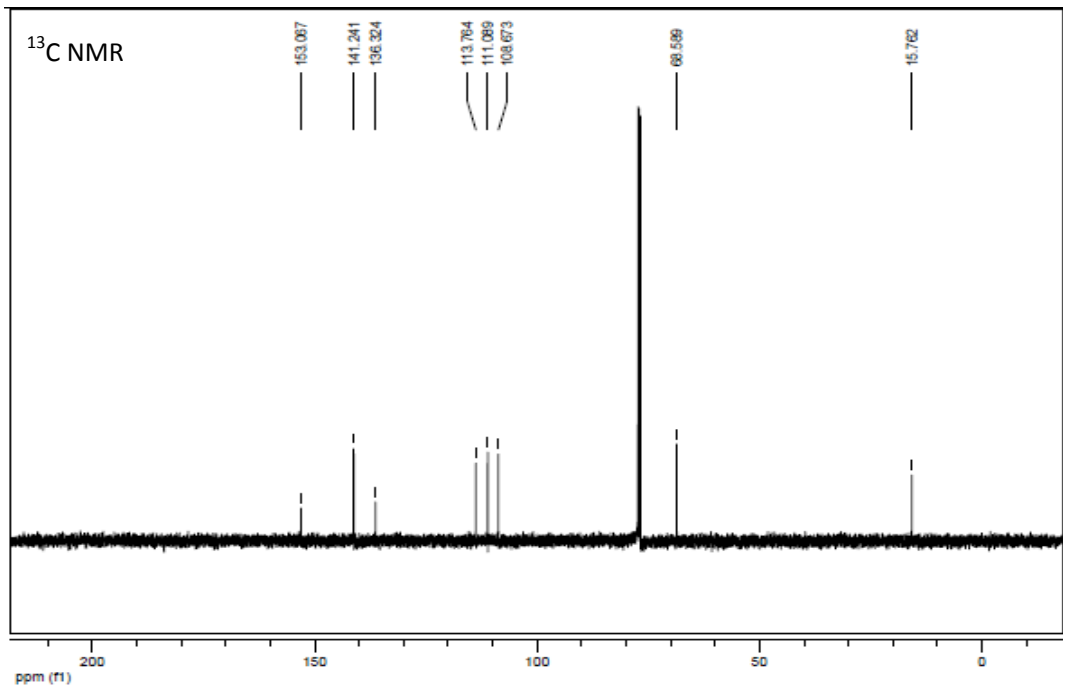


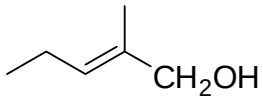




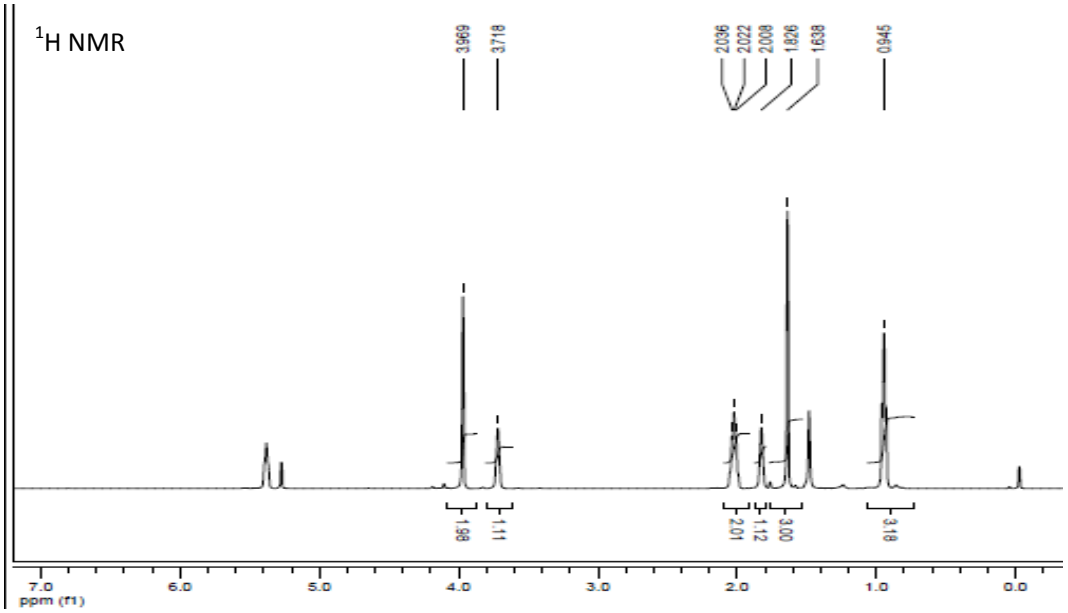
(entry 6, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 1.69 (s, 1H; OH), 1.99 (s, 3H; CH_3), 4.14 (s, 2H; CH_2), 6.25-6.38 (m, 3H), 7.35 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 15.75, 68.59, 108.67, 111.09, 113.76, 136.32, 141.24, 153.06 ppm; FT-IR (film): ν_{max} = 3337, 2916, 2857, 1491, 1066, 1015 cm^{-1}; MS (EI): m/z (%) 138 $[M]^{+}$ (90), 81 (100), 68 (60), 77 (50), 95 (50).

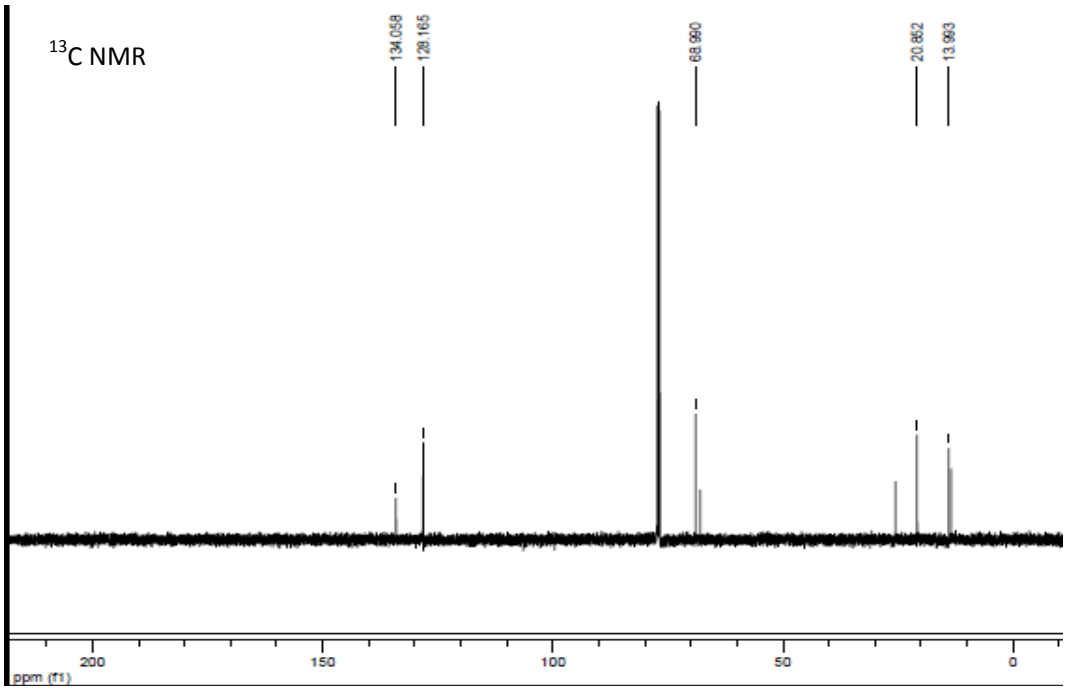


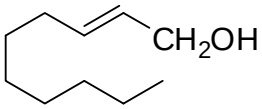




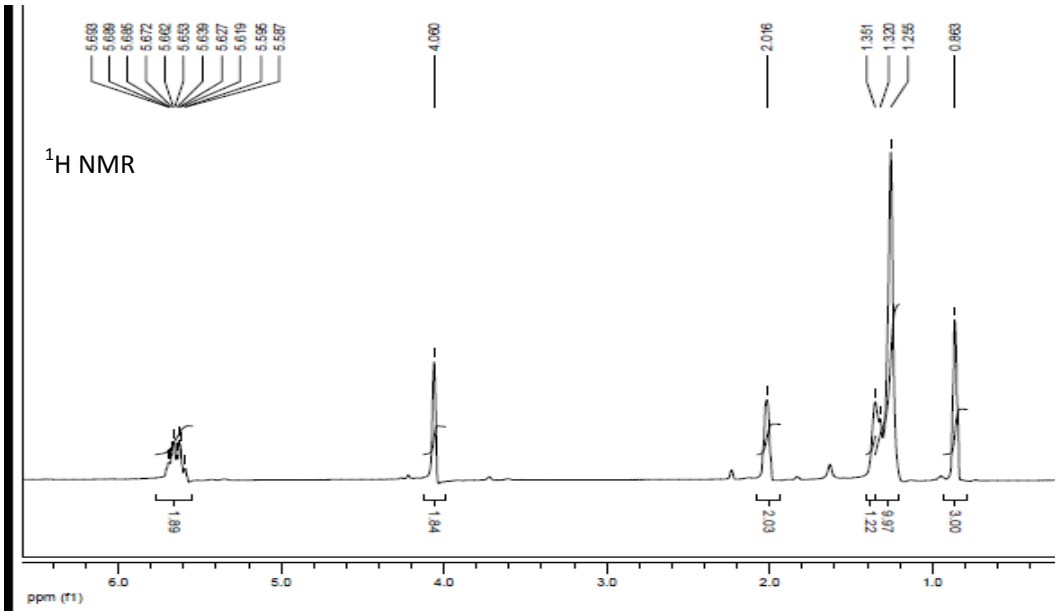
(entry 7, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 0.94 (m, 3H; CH_3), 1.63 (s, 3H; CH_3), 1.82 (s, 1H; CH), 3.71 (s, 1H; OH), 3.96 (s, 2H; CH_2); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 13.99, 20.85, 68.99, 128.16, 134.06 ppm; FT-IR (film): ν_{max} = 3337, 2916, 2857, 1066, 1015 cm^{-1}; MS (EI): m/z (%) 100 $[M]^+$ (45), 71 (100), 43 (90), 57 (40), 69 (40).

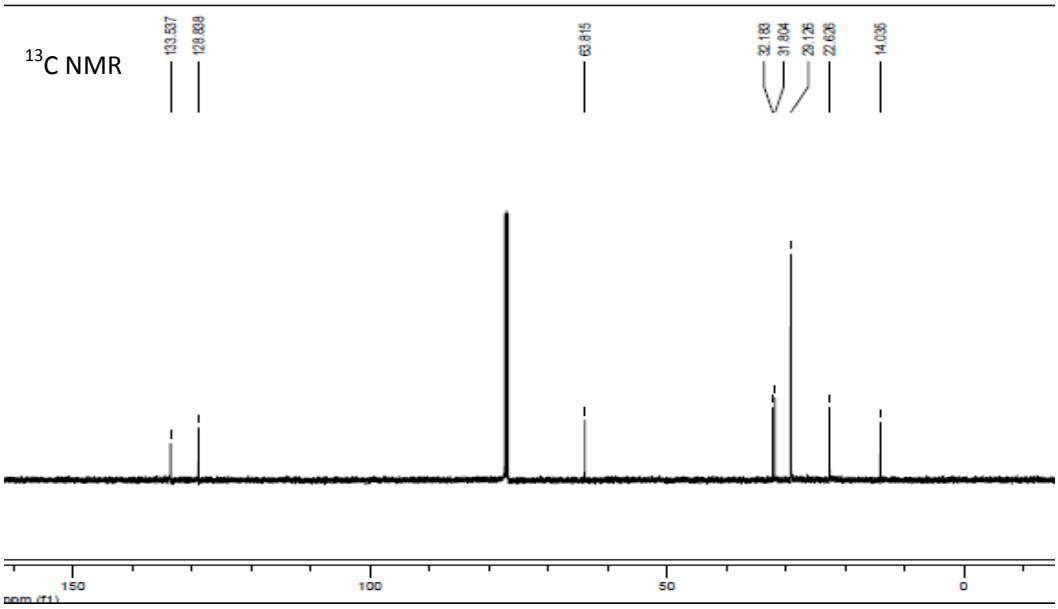


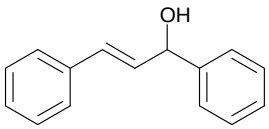




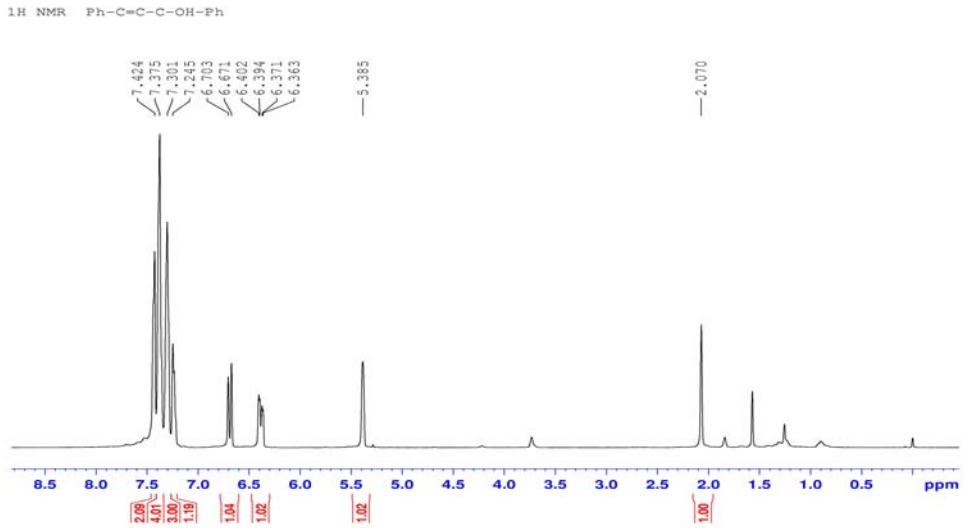
(entry 8, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 0.86 (m, 3H; CH_3), 1.25 (s, 10H), 1.32 (s, 1H; OH), 2.06 (m, 2H; CH_2), 4.06 (s, 2H; CH_2), 5.58-5.69 (m, 2H; CH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 14.03, 22.62. 29.13, 31.80, 32.18, 63.81, 128.83, 133.53 ppm; FT-IR (film): ν_{max} = 3347, 2956, 2925, 2855, 1465, 969 cm^{-1}; MS (EI): m/z (%) 156[M]$^{+}$ (1), 57 (100), 43 (50), 67 (40), 29 (30).

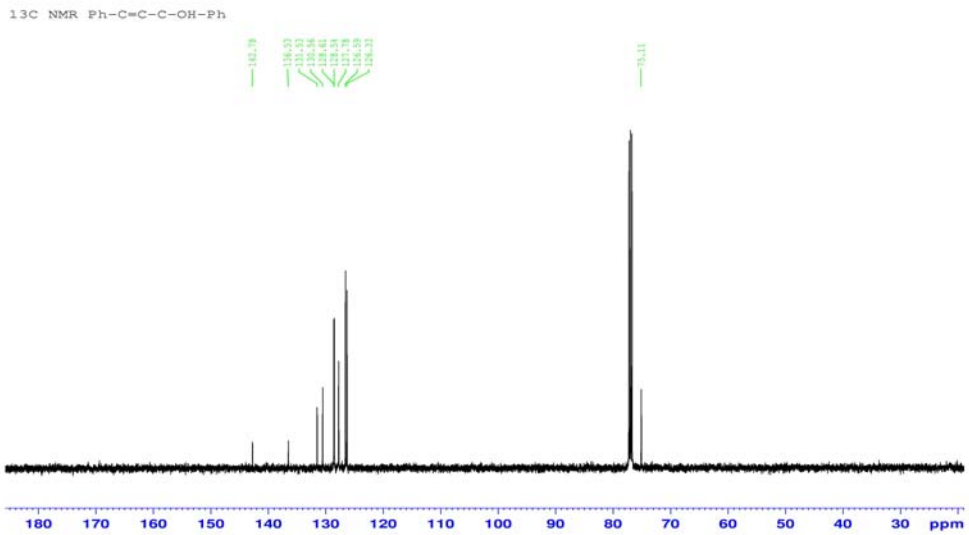


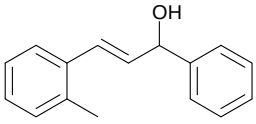




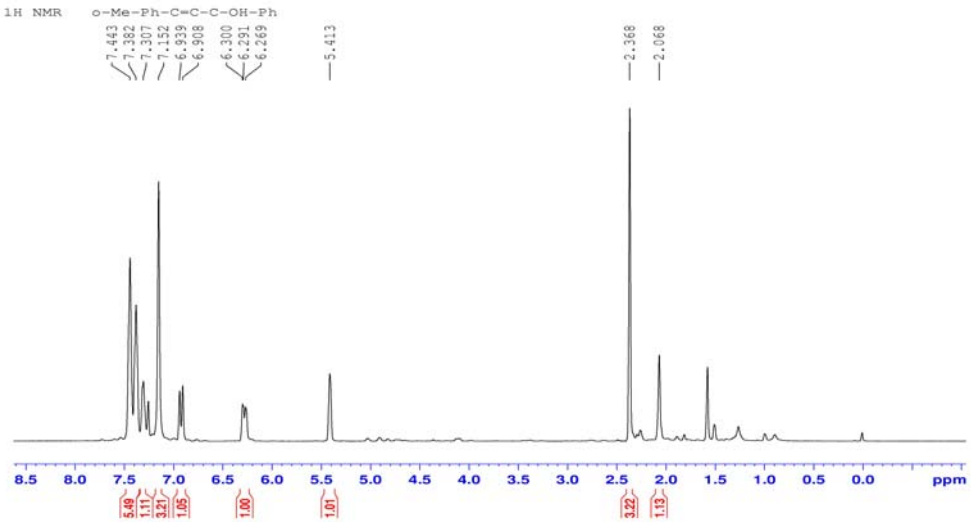
(entry 9, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 2.07 (s, 1H; OH), 5.38 (s, 1H; CH), 6.36-6.40 (m, 1H; CH), 6.68 (d, $^{3}J_{HH}$ = 15.80 Hz, 1H; CH), 7.24-7.42 ppm (m, 10H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 75.11, 126.32, 126.59, 127.75, 127.77, 128.54, 128.60, 130.56, 131.51, 136.53, 142.78 ppm ; FT-IR (film): ν_{max} = 3342, 3077, 3059, 3027, 1599, 1449, 1493, 1092, 1067, 1009, 966, 744, 695 cm^{-1}; MS (EI): m/z (%) 209 $[M-H]^{+}$ (47), 105 (100), 191 (67), 178 (27), 77 (33), 115 (30).

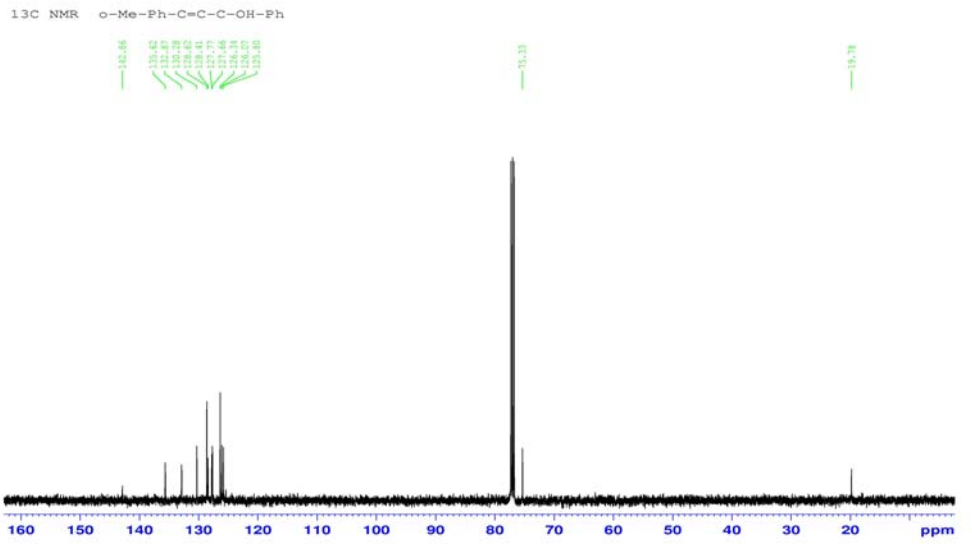


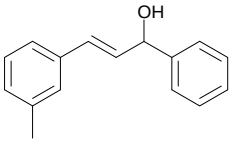




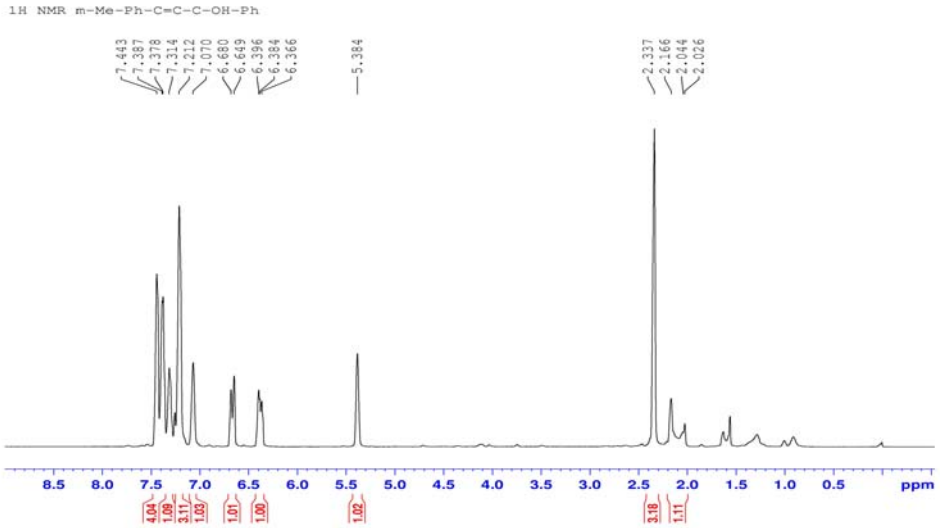
(entry 10, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 2.07 (s, 1H; OH), 2.37 (s, 3H; CH_3), 5.41 (s, 1H; CH), 6.30-6.40 (m, 1H; CH), 6.92 (d, $^{3}J_{HH}$ = 15.60 Hz, 1H; CH), 7.15-7.44 ppm (m, 9H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 19.78, 75.33, 125.79, 126.06, 126.34, 127.65, 127.77, 128.41, 128.61, 130.28, 132.87, 135.62, 142.86 ppm ; FT-IR (film): ν_{max} = 3349, 3061, 3062, 2969, 2863, 1601, 1487, 1463cm^{-1}; MS (EI): m/z (%) 224 $[M]^{+}$ (3), 105 (100), 206 (16), 77 (26)

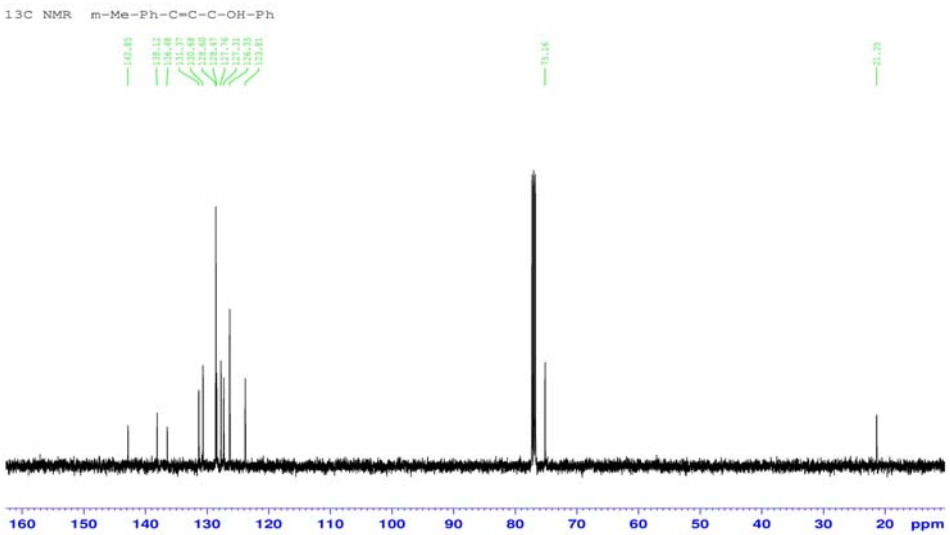


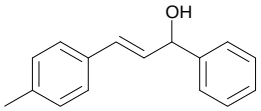




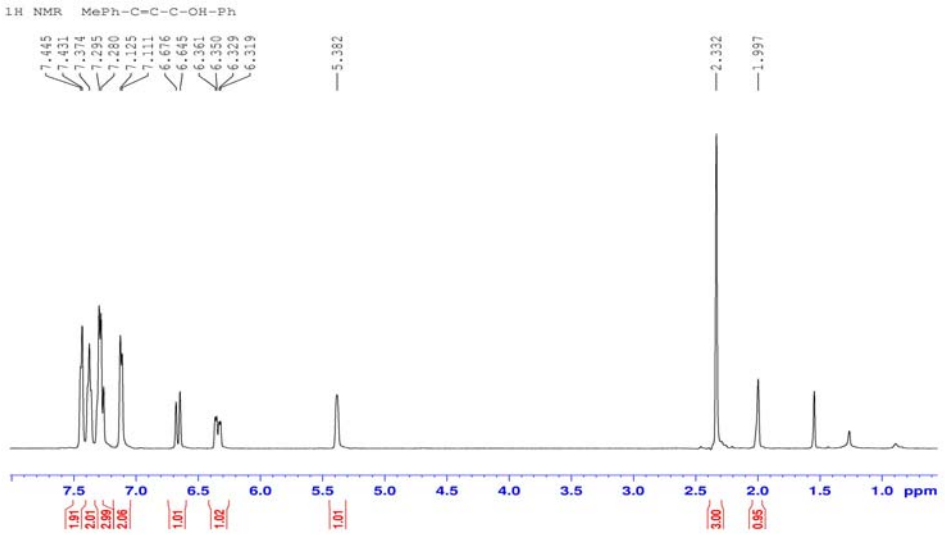
(entry 11, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 2.16 (s, 1H; OH), 2.34 (s, 3H; CH_3), 5.38 (s, 1H; CH), 6.37-6.40 (m, 1H; CH), 6.66 (d, $^{3}J_{HH}$ = 15.55 Hz, 1H; CH), 7.07-7.44 ppm (m, 9H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 21.35, 75.16, 123.81, 126.34, 127.30, 127.76, 128.46, 128.60, 130.68, 131.36, 136.48, 138.11, 142.85 ppm ; FT-IR (film): ν_{max} = 3350, 3056, 3028, 2955, 2919, 2862, 1602, 1491, 1453 cm^{-1}; MS (EI): m/z (%) 224 $[M]^{+}$ (15), 105 (100), 119 (36), 77 (33).

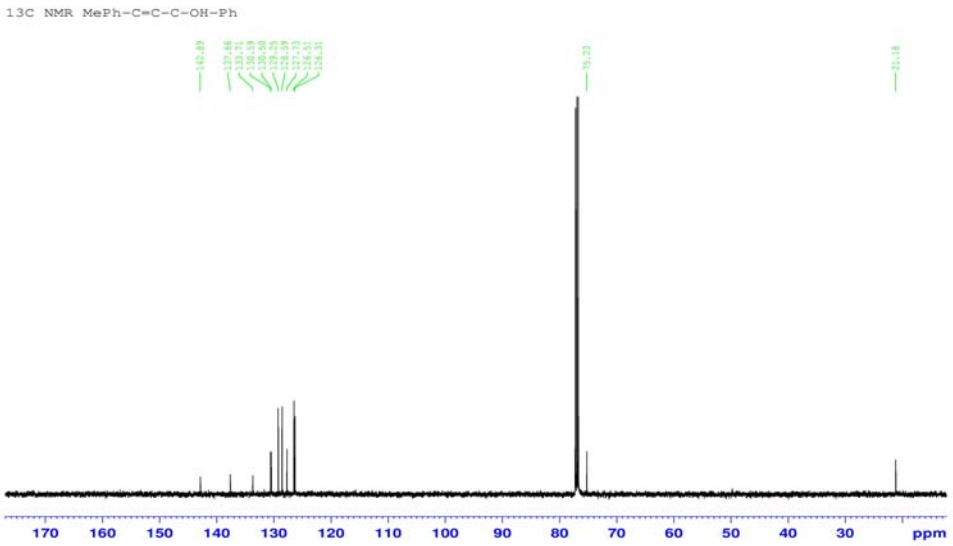


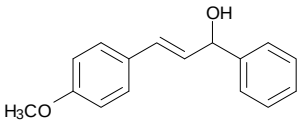




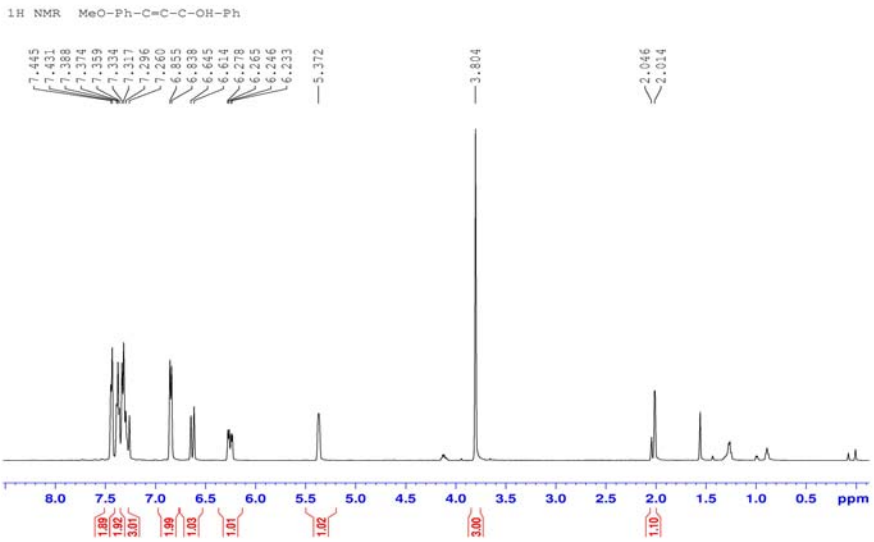
(entry 12, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 1.99 (s, 1H; OH), 2.33 (s, 3H; CH_3), 5.38 (s, 1H; CH), 6.31-6.36 (m, 1H; CH), 6.66 (d, $^{3}J_{HH}$ = 15.80 Hz, 1H; CH), 7.11-7.44 ppm (m, 9H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 21.71, 75.23, 126.31, 126.51, 127.73, 128.58, 129.25, 130.50, 130.59, 133.78, 137.66, 142.88 ppm; FT-IR (film): ν_{max} = 3342, 2081, 3026, 2919, 2859, 1513, 1493, 1451 cm^{-1}; MS (EI): m/z (%) 223 $[M\text{-}H]^{+}$ (47), 105 (100), 207 (50), 119 (60), 77 (40).

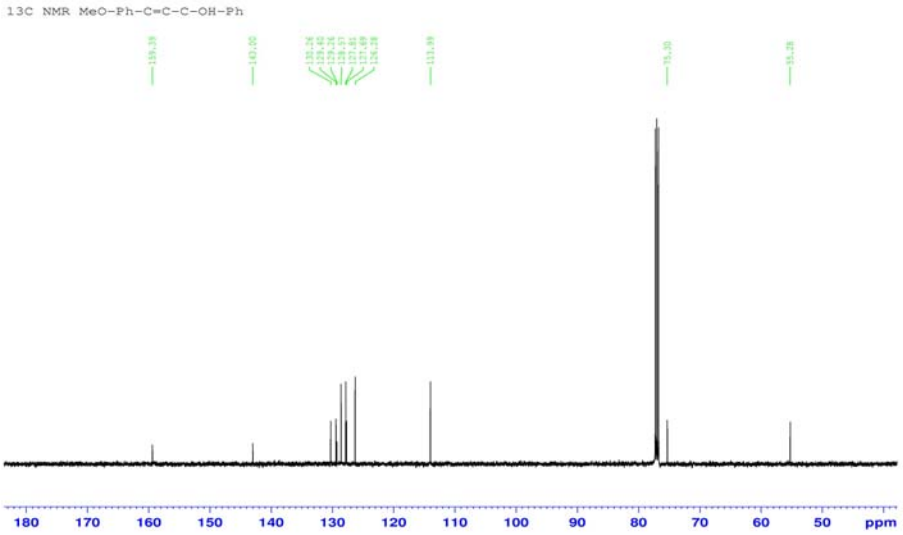


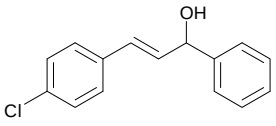




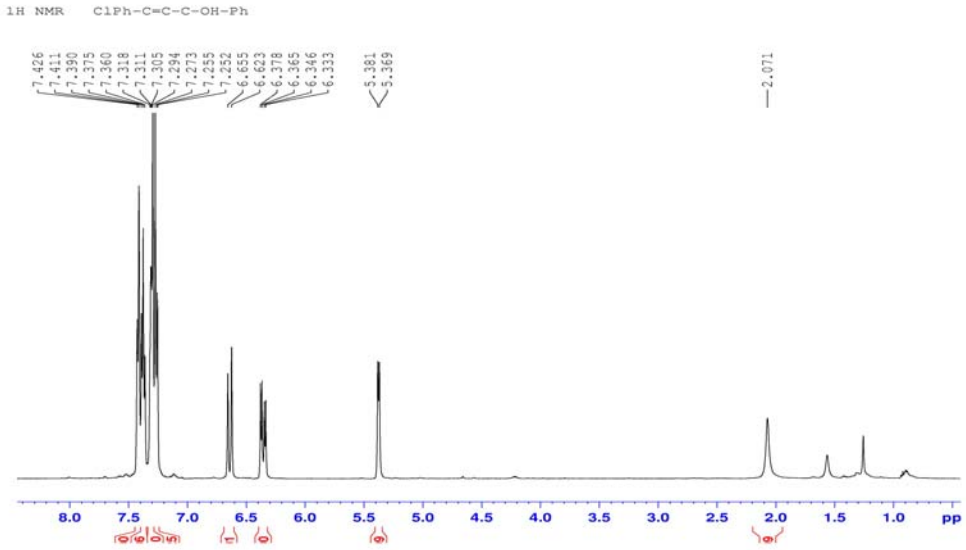
(entry 13, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 2.04 (s, 1H; OH), 3.80 (s, 3H; CH_3), 5.37 (s, 1H; CH), 6.23-6.27 (m, 1H; CH), 6.63 (d, $^{3}J_{HH}$ = 15.80 Hz, 1H; CH), 6.84 (d, $^{3}J_{HH}$ = 8.35 Hz, 2H; ArH), 7.29-7.44 ppm (m, 7H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 55.27, 75.30, 113.98, 126.28, 127.69, 127.81, 128.57, 129.26, 129.40, 130.26, 142.99, 159.38 ppm ; FT-IR (film): ν_{max} = 3374, 3060, 3030, 3005, 2956, 2935, 2836, 1606, 1511, 1250 cm^{-1}; MS (EI): m/z (%) 239 $[M-H]^{+}$ (43), 121 (100), 222 (36), 178 (36), 77 (38), 105 (37).

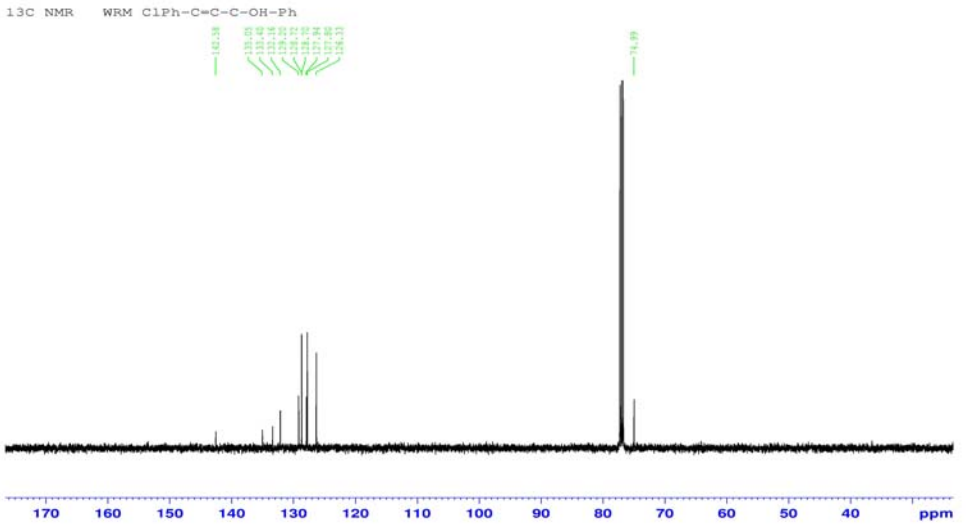


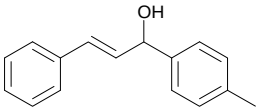




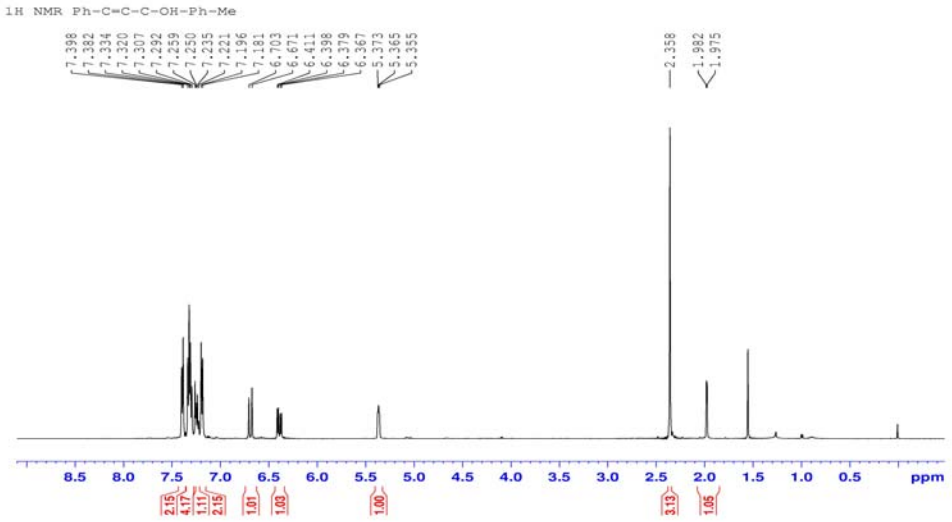
(entry 14, Table 2): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 2.07 (s, 1H; OH), 5.37 (d, $^{3}J_{HH}$ = 6 Hz, 1H; CH), 6.33-6.37 (m, 1H; CH), 6.64 (d, $^{3}J_{HH}$ = 15.80 Hz, 1H; CH), 7.25-7.42 ppm (m, 9H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 74.99, 126.32, 127.79, 127.93, 128.69, 128.71, 129.19, 132.16, 133.40, 135.05, 142.58 ppm; FT-IR (film): ν_{max} = 3338, 3060, 3029, 2958, 2924, 2856, 1593, 1491, 1452, 1404 cm^{-1}; MS (EI): m/z (%) 244 $[M]^{+}$ (37), 105 (100), 139 (32), 190 (27), 77 (33).

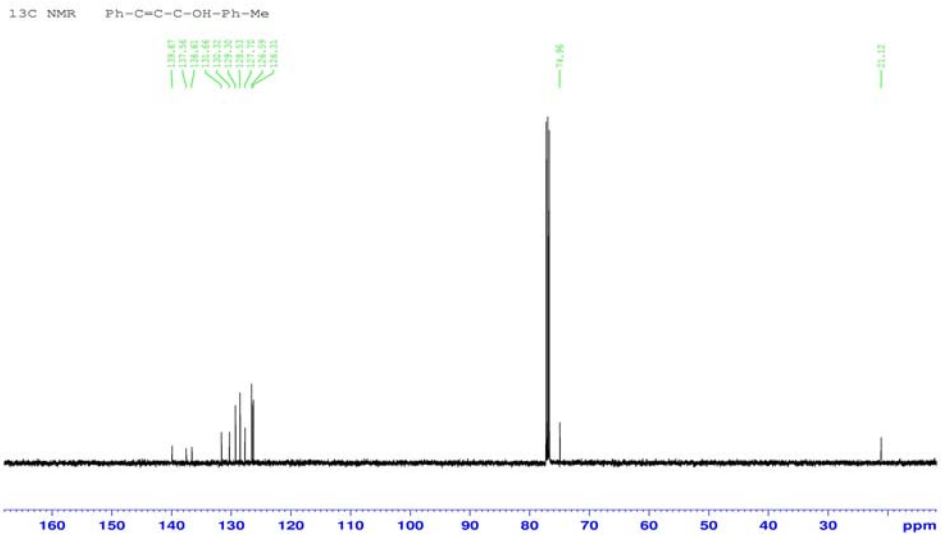


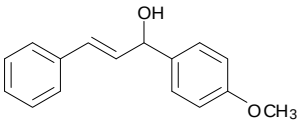




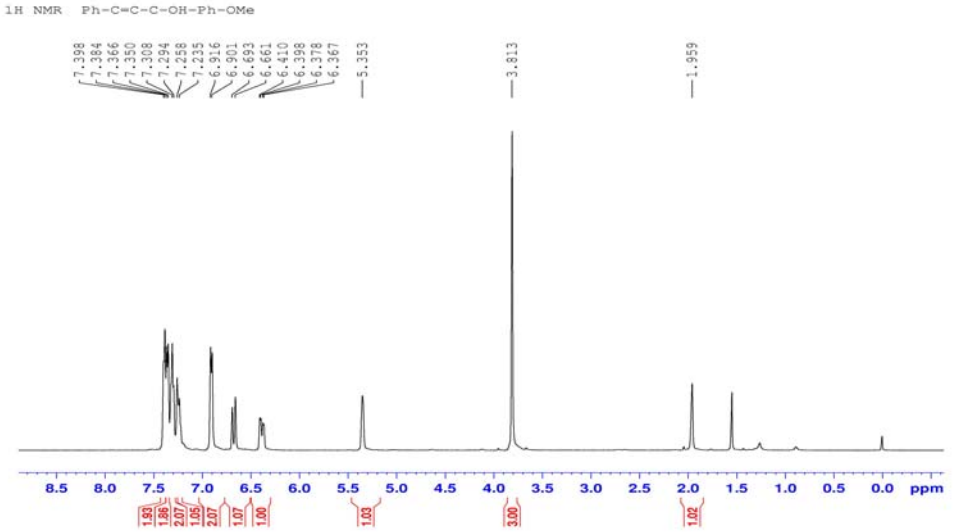
(entry 15, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 1.98 (d, $^{3}J_{HH}$ = 3.45 Hz, 1H; OH), 2.35 (s, 3H; CH_3), 5.36 (t, $^{3}J_{HH}$ = 4.52 Hz, 1H; CH), 6.36-6.41 (m, 1H; CH), 6.68 (d, $^{3}J_{HH}$ = 15.85 Hz, 1H; CH), 7.18-7.39 ppm (m, 9H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 21.11, 74.96, 136.31, 126.58, 127.70, 128.53, 129.30, 130.31, 131.66, 136.60, 137.56, 139.86 ppm; FT-IR (film): v_{max} = 3338, 3083, 3026, 2971, 2919, 1599, 1578, 1509 cm^{-1}; MS (EI): m/z (%) 223 $[M-H]^{+}$ (47), 119 (100), 206 (98), 105 (60), 191 (70), 77 (40).

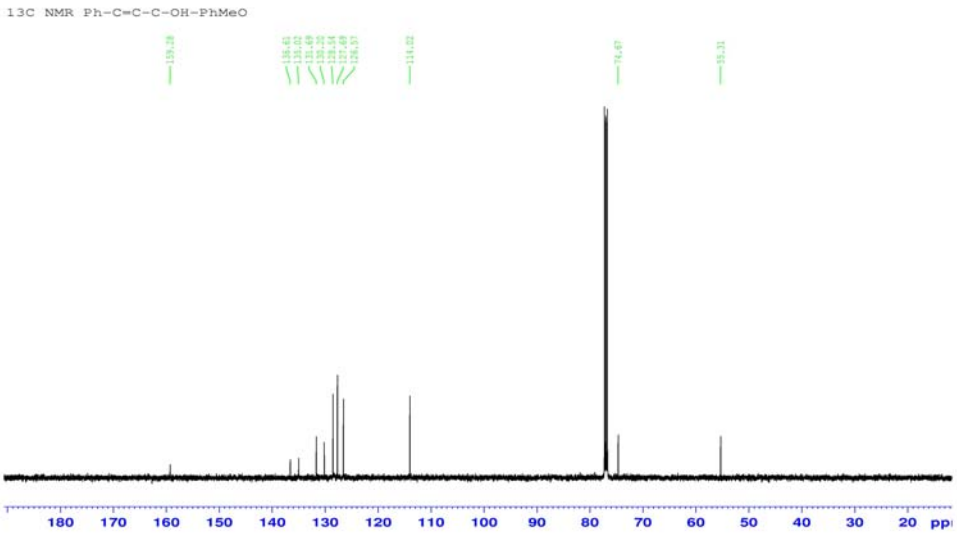


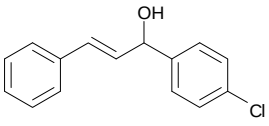




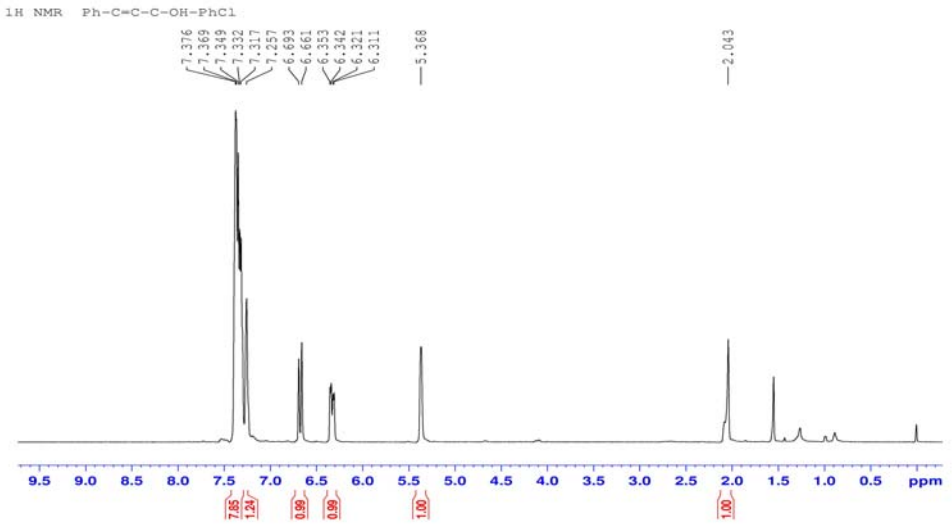
(entry 16, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 1.96 (s, 1H; OH), 3.81 (s, 3H; CH_3), 5.35 (s, 1H; CH), 6.36-6.41 (m, 1H; CH), 6.67 (d, $^{3}J_{HH}$ = 15.85 Hz, 1H; CH), 6.91 (d, $^{3}J_{HH}$ = 7.90 Hz, 2H; ArH), 7.23-7.39 ppm (m, 7H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 55.31, 74.66, 114.01, 126.57, 127.69, 128.54, 130.20, 131.69, 135.01, 136.61, 159.28 ppm; FT-IR (film): ν_{max} = 3379, 3059, 3026, 2956, 2908, 2835, 1610, 1511, 1449 cm^{-1}; MS (EI): m/z (%) 239 $[M-H]^{+}$ (43), 223 (100), 135 (85), 178 (50), 77 (35).

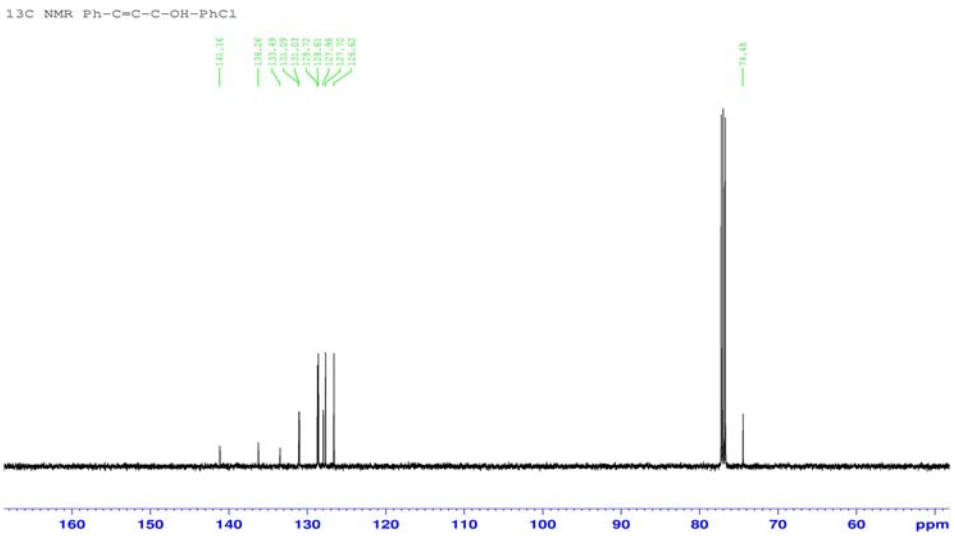


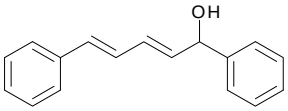




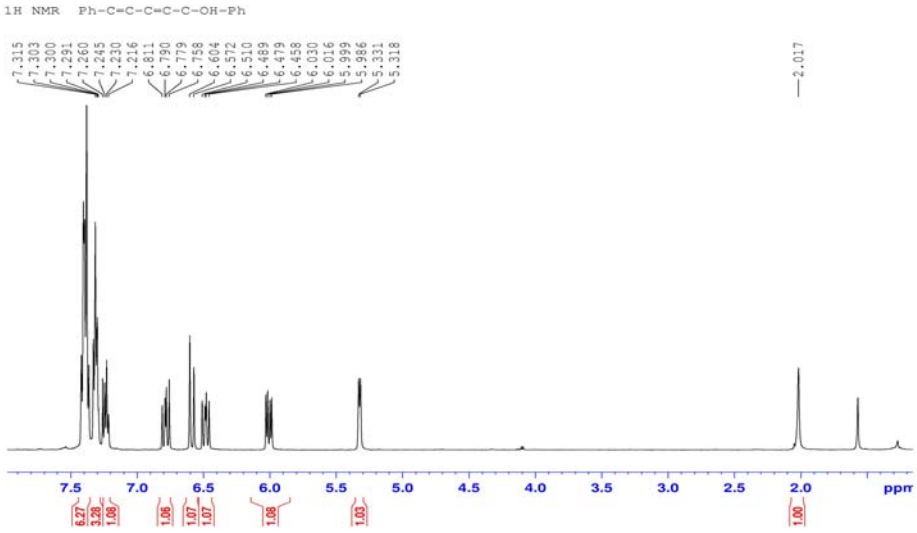
(entry 17, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 2.04 (s, 1H; OH), 5.37 (s, 1H; CH), 6.31-6.35 (m, 1H; CH), 6.67 (d, $^{3}J_{HH}$ = 15.80 Hz, 1H; CH), 7.25-7.27 ppm (m, 9H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 74.48, 126.62, 127.69, 127.97, 128.61, 128.71, 131.03, 131.08, 133.49, 136.25, 141.16 ppm; FT-IR (film): ν_{max} = 3334, 3078, 3059, 3027, 2957, 2925, 2870, 1597, 1490, 1449, 1404 cm^{-1}; MS (EI): m/z (%) 244 $[M]^{+}$ (36), 139 (100), 105 (60), 192 (60), 77 (33).

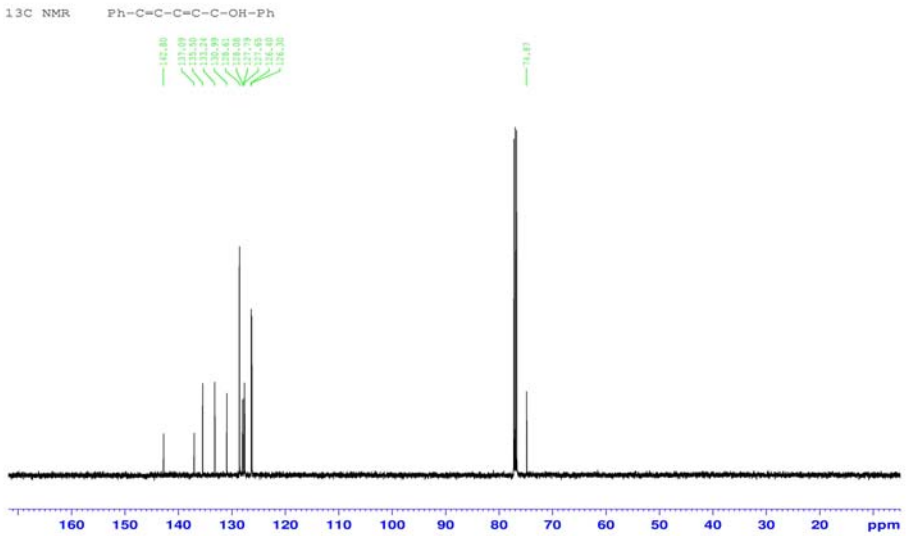


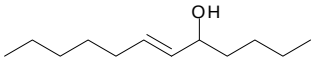




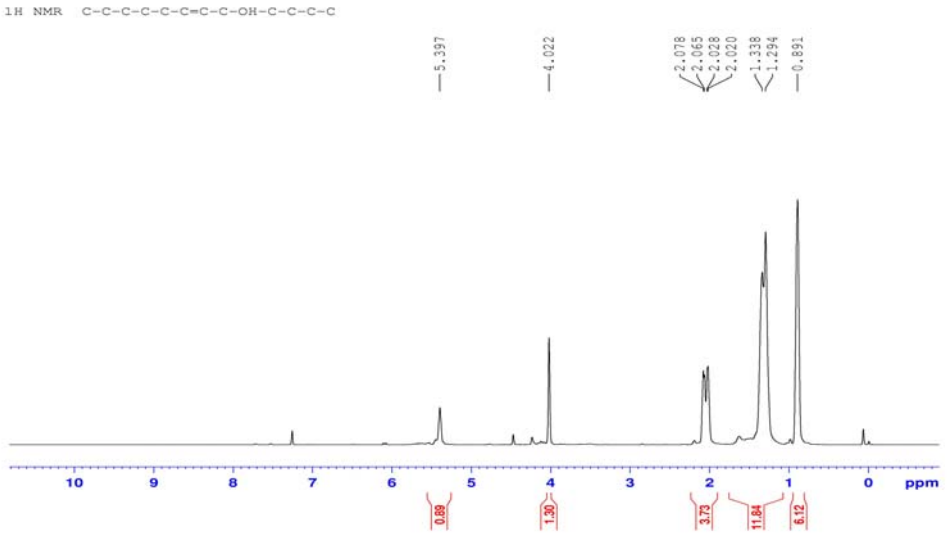
(entry 18, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 2.01 (s, 1H; OH), 5.32 (d, $^{3}J_{HH}$ = 6.35 Hz, 1H; CH), 5.98-6.02 (m, 1H; CH), 6.45-6.50 (m, 1H; CH), 6.58 (d, $^{3}J_{HH}$ = 15.65 Hz, 1H; CH), 6.75-6.81 (m, 1H; CH), 7.21-7.42 ppm (m, 10H; ArH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 74.86, 126.30, 126.39, 127.65, 127.78, 128.07, 128.60, 130.98, 133.23, 135.49, 137.08, 142.79 ppm; FT-IR (film): ν_{max} = 3290, 3080, 3059, 3026, 1599, 1492, 1449 cm^{-1}; MS (EI): m/z (%) 235 $[M-H]^{+}$ (25), 105 (100), 217 (90), 128 (50), 202 (50), 77 (33).

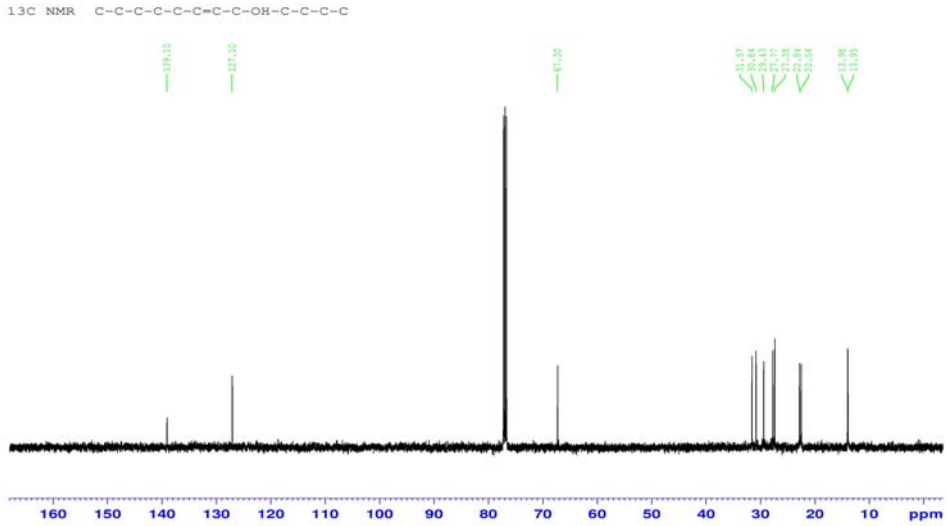


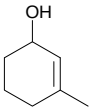




(entry 19, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 0.8 (s, 6H), 1.29-1.33 (m, 12H), 2.01-2.07 (m, 4H), 4.02 (s, 2H; OH), 5.39 ppm (s, 1H; CH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 13.94, 13.98, 22.53, 22.84, 27.38, 27.76, 29.42, 30.83, 31.56, 67.30, 127.09, 139.09 ppm; FT-IR (film): ν_{max} = 3344, 2928, 2397, 1378, 1331, 1086 cm^{-1}; MS (EI): m/z (%) 184 $[M]^{+}$ (9), 57 (100), 81 (39), 71 (76), 94 (35).







(entry 20, Table 1): ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C; TMS): δ = 1.38 (s, 1H; CH), 1.55-1.61 (m, 2H, CH_2), 1.68 (s, 3H; CH_3), 1.72-1.92 (m, 4H), 4.17 (s, 1H; OH), 5.49 (s, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$, 25^{o}C; $CDCl_3$) : δ = 18.89, 23.60, 30.06, 31.67, 65.86, 124.23, 138.72 ppm; FT-IR (film): ν_{max} = 3342, 2935, 2862, 1447, 1376, 1033 cm^{-1}; MS (EI): m/z (%) 112 $[M]^{+}$ (30), 97 (100), 79 (80), 69 (25).