

Supporting Information

Nano titania-supported sulfonic acid catalyzed synthesis of α,α' -bis(substituted-benzylidene)cycloalkanones and their xanthene derivatives under solvent-free conditions

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Materials and Instruments

Chemicals were purchased from the Merck chemical companies. Thin-Layer Chromatography (TLC) on commercial plates of silica gel 60 F254 was used to monitor the progress of reactions. The products were characterized by FT-IR spectra, ^1H NMR, ^{13}C NMR. FT-IR spectra were recorded on Shimadzo FT-IR 8400 instrument. ^1H and ^{13}C NMR spectra were recorded on Bruker Advance Spectrometer 300 MHz and 75 MHz respectively, using CDCl_3-d as solvent. The chemical shifts are expressed in parts per million (ppm) and tetramethylsilane (TMS) was used as an internal reference. Melting points were recorded on a THERMO SCIENTIFIC 9100 apparatus.

General procedure for the synthesis of α,α' -bis(substituted-benzylidene)cycloalkanones (3)

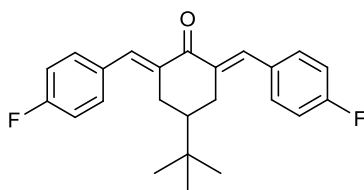
A mixture of cyclohexanone (1 mmol), aromatic aldehyde (2 mmol) and 0.032 g n-TSA was stirred at 90 °C under solvent-free condition for an appropriate time. After completion of the reaction (monitored by TLC), hot ethanol was added and the catalyst was filtered. The title compounds were obtained in their yellowish crystalline forms by recrystallization of ethanol solution.

General procedure for the synthesis of xanthenes (5)

A mixture of α,α' -Bis(substituted-benzylidene)cycloalkanones (1 mmol), dimedone (1 mmol) and 0.012 g n-TSA was added in a test tube and heated in an oil bath at 130 °C under solvent-free condition for an appropriate time. After completion of the reaction (monitored by TLC), hot ethanol was added and the catalyst was filtered. The products were obtained in white powder by recrystallization of ethanol solution.

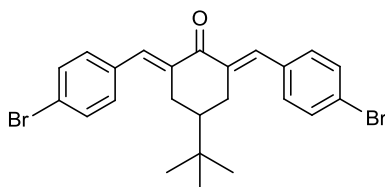
Characterization Data for new compounds

2,6-bis(4-fluorobenzylidene)-4-(tert-butyl)cyclohexanone (Table 2, entry 18)



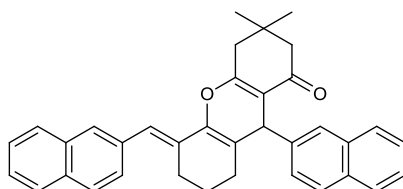
Yellow crystal; m.p. = 174-177 °C; IR (KBr) (cm^{-1}) ν_{max} : 2956, 2869, 1664, 1602, 1508, 1155; ^1H NMR (300 MHz, CDCl_3) 0.95 (s, 9H), 1.47 (tt, $J=12.7\text{Hz}/2.8\text{Hz}$, 1H), 2.41 (m, 2H), 3.11 (dd, $J=15.6\text{Hz}/2.3\text{Hz}$, 2H), 7.73 (s, 2H), 7.08-7.47 (m, 8H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 27.23, 29.37, 32.49, 44.32, 115.45, 115.73, 132.02, 132.06, 132.11, 132.22, 135.65, 135.68, 135.78, 160.94, 164.26, 190.22.

2,6-bis(4-bromobenzylidene)-4-(tert-butyl)cyclohexanone (Table 2, entry 19)



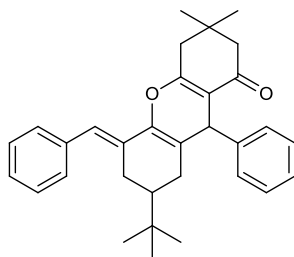
Yellow crystal; m.p. = 161-164 °C; IR (KBr) (cm^{-1}) ν_{max} : 2958, 2867, 1662, 1604, 1487, 1074; ^1H NMR (300 MHz, CDCl_3) 0.94 (s, 9H), 1.47 (tt, $J=12.8\text{Hz}/3.2\text{Hz}$, 1H), 2.40 (m, 2H), 3.09 (dd, $J=15.5\text{Hz}/2.3\text{Hz}$, 2H), 7.68 (s, 2H), 7.30-7.56 (m, 8H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 27.22, 29.42, 32.51, 44.26, 122.89, 131.71, 134.73, 135.76, 136.48, 190.06.

(E)-3,3-dimethyl-9-(naphthalen-2-yl)-5-(naphthalen-2-ylmethylene)-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one (Table 7, entry 13)



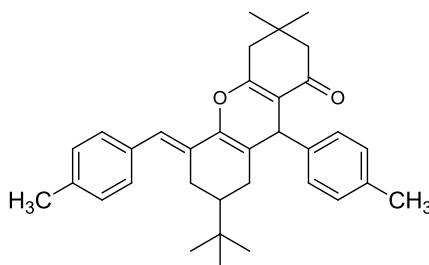
White powder; m.p. = 208-210 °C; IR (KBr) (cm^{-1}) ν_{max} : 3421, 3051, 2941, 1622, 1660, 1220, 748; ^1H NMR (300 MHz, CDCl_3) 1.04 (s, 3H), 1.15 (s, 3H), 1.65 (m, 2H), 2.17 (m, 4H), 2.66 (m, 3H), 2.86 (m, 1H), 4.42 (s, 1H), 7.16 (s, 1H), 7.39-7.84 (m, 14H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 22.46, 27.31, 27.42, 27.75, 29.39, 32.18, 40.53, 41.39, 50.82, 112.42, 118.30, 122.20, 125.40, 125.83, 126.17, 126.54, 127.02, 127.53, 127.60, 127.92, 128.01, 128.08, 130.67, 132.12, 132.49, 133.27, 133.40, 134.90, 141.47, 142.01, 164.13, 197.22.

(E)-5-benzylidene-7-(tert-butyl)-3,3-dimethyl-9-phenyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one (Table 7, entry 14)



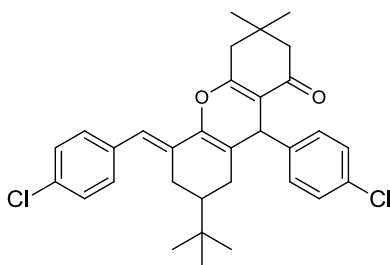
White powder; m.p. = 173-176 °C; IR (KBr) (cm^{-1}) ν_{max} : 3024, 2956, 1660, 1627, 1380, 1340, 1224, 769; ^1H NMR (300 MHz, CDCl_3) 0.78 (s, 9H), 1.00 (s, 3H), 1.10 (s, 3H), 1.25 (m, 1H), 1.96 (m, 2H), 2.18 (m, 3H), 2.52 (m, 2H), 3.03 (dd, $J=14.70\text{Hz}/2.76\text{Hz}$, 1H), 4.23 (s, 1H), 6.93 (s, 1H), 7.15-7.40 (m, 8H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 27.14, 27.23, 27.33, 27.91, 28.22, 29.33, 32.15, 32.18, 39.69, 41.36, 43.86, 50.82, 112.65, 118.39, 121.80, 126.46, 126.50, 128.19, 128.42, 129.21, 130.95, 137.43, 142.18, 143.97, 164.30, 197.19.

(E)-7-(tert-butyl)-3,3-dimethyl-5-(4-methylbenzylidene)-9-(p-tolyl)-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one (Table 7, entry 15)



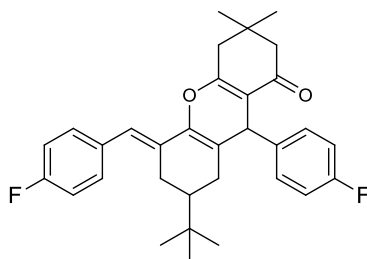
White powder; m.p. = 207-212 °C; IR (KBr) (cm^{-1}) ν_{max} : 3020, 2952, 1662, 1629, 1379, 1365, 1110, 833; ^1H NMR (300 MHz, CDCl_3) 0.78 (s, 9H), 1.00 (s, 3H), 1.10 (s, 3H), 1.25 (m, 1H), 1.99 (m, 2H), 2.20 (m, 3H), 2.26 (s, 3H), 2.37 (s, 3H), 2.53 (m, 2H), 3.04 (d, $J=6.3\text{Hz}$, 1H), 4.18 (s, 1H), 6.89 (s, 1H), 7.04-7.26 (m, 8H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 21.08, 21.21, 27.18, 27.27, 27.38, 27.47, 27.86, 28.24, 29.33, 32.15, 32.21, 39.24, 40.56, 41.37, 43.76, 50.85, 112.78, 117.80, 118.16, 121.58, 127.96, 128.26, 128.87, 128.92, 129.01, 129.14, 130.34, 130.59, 134.56, 135.81, 135.91, 136.20, 141.01, 141.14, 163.74, 164.24, 197.23.

(E)-7-(tert-butyl)-5-(4-chlorobenzylidene)-9-(4-chlorophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one (Table 7, entry 16)



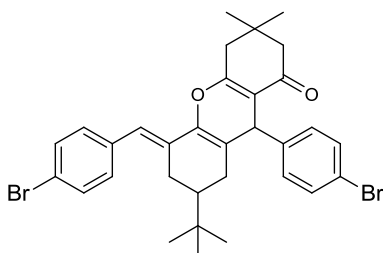
White powder; m.p. = 249-253 °C; IR (KBr) (cm^{-1}) ν_{max} : 2960, 1662, 1627, 1379, 1089; ^1H NMR (300 MHz, CDCl_3) 0.77 (s, 9H), 0.98 (s, 3H), 1.10 (s, 3H), 1.25 (m, 1H), 1.98 (m, 2H), 2.20 (m, 3H), 2.53 (m, 2H), 2.96 (dd, $J=14.65\text{Hz}/2.78\text{Hz}$, 1H), 4.21 (s, 1H), 6.86 (s, 1H), 7.23-7.35 (m, 8H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 27.12, 27.20, 27.28, 27.91, 28.14, 29.30, 32.16, 32.18, 39.16, 41.32, 43.88, 50.75, 112.33, 118.19, 120.94, 128.40, 128.51, 129.48, 129.77, 130.43, 131.35, 132.18, 132.30, 135.75, 142.27, 142.44, 163.81, 164.33, 197.11.

(E)-7-(tert-butyl)-5-(4-fluorobenzylidene)-9-(4-fluorophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one (Table 7, entry 17)



White powder; m.p. = 228-233 °C; IR (KBr) (cm^{-1}) ν_{max} : 2958, 1652, 1600, 1380, 1222, 1157; ^1H NMR (300 MHz, CDCl_3) 0.77 (s, 9H), 0.99 (s, 3H), 1.11 (s, 3H), 1.24 (m, 1H), 1.95 (m, 2H), 2.18 (m, 3H), 2.52 (m, 2H), 2.96 (dd, $J=14.63\text{Hz}/2.83\text{Hz}$, 1H), 4.22 (s, 1H), 6.88 (s, 1H), 6.91-7.30 (m, 8H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 27.10, 27.27, 27.86, 28.12, 29.29, 32.16, 38.94, 41.33, 43.95, 50.78, 112.55, 114.84, 115.02, 115.13, 115.31, 118.09, 120.93, 129.80, 129.90, 130.67, 130.70, 130.77, 133.32, 133.37, 139.67, 139.71, 142.20, 159.81, 159.89, 163.08, 164.22, 197.17.

(E)-7-(tert-butyl)-5-(4-bromobenzylidene)-9-(4-bromophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one (Table 7, entry 18)



White powder; m.p. = 250-254 °C; IR (KBr) (cm^{-1}) ν_{max} : 3056, 2866, 1658, 1625, 1380, 1064; ^1H NMR (300 MHz, CDCl_3) 0.79 (s, 9H), 0.98 (s, 3H), 1.12 (s, 3H), 1.26 (m, 1H), 2.03 (m, 2H), 2.18 (m, 3H), 2.53 (m, 2H), 2.80 (m, 1H), 4.20 (s, 1H), 6.95 (s, 1H), 7.16-7.35 (m, 8H, ArH); ^{13}C NMR (75 MHz, CDCl_3): δ 26.60, 27.05, 28.04, 30.40, 32.31, 33.04, 39.59, 41.93, 43.93, 50.77, 113.57, 118.04, 121.13, 128.32, 128.43, 129.72, 130.48, 130.53, 132.27, 132.37, 135.67, 141.93, 142.60, 165.75, 197.33.

Copies of FT-IR, ¹H NMR and ¹³C NMR Spectra

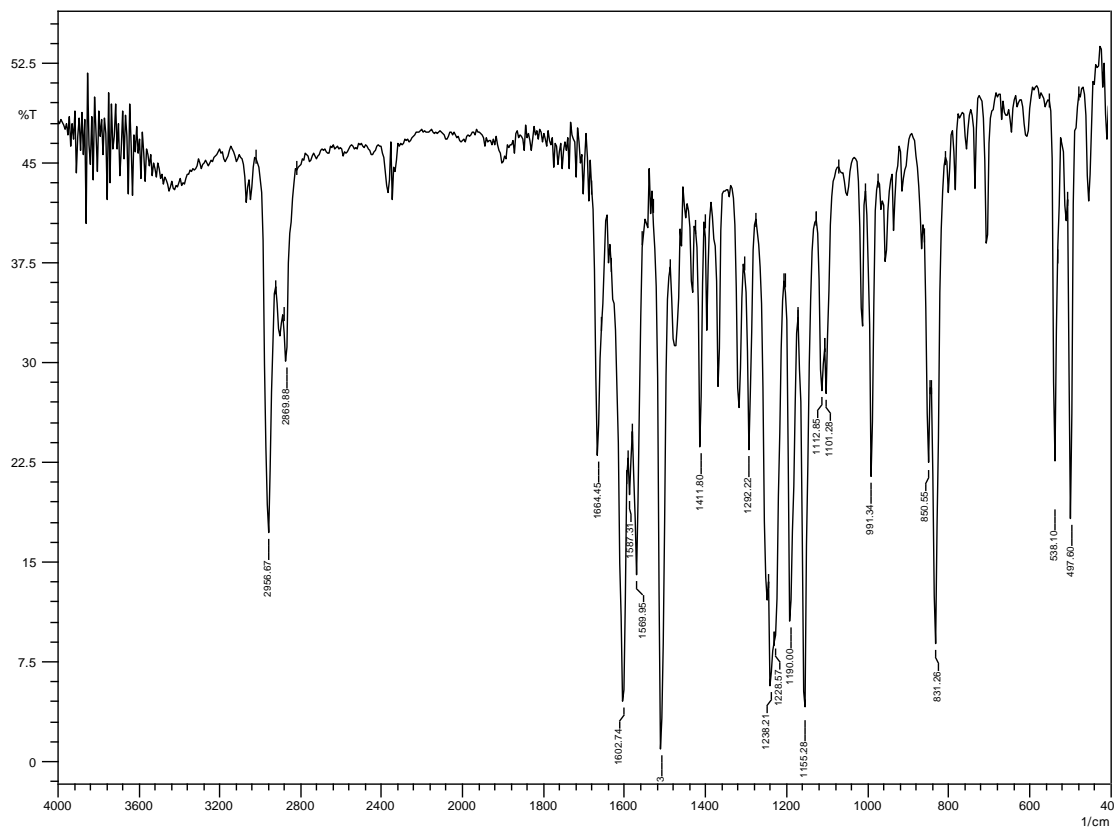


Fig. 1. FT-IR of 2,6-bis(4-fluorobenzylidene)-4-(tert-butyl)cyclohexanone

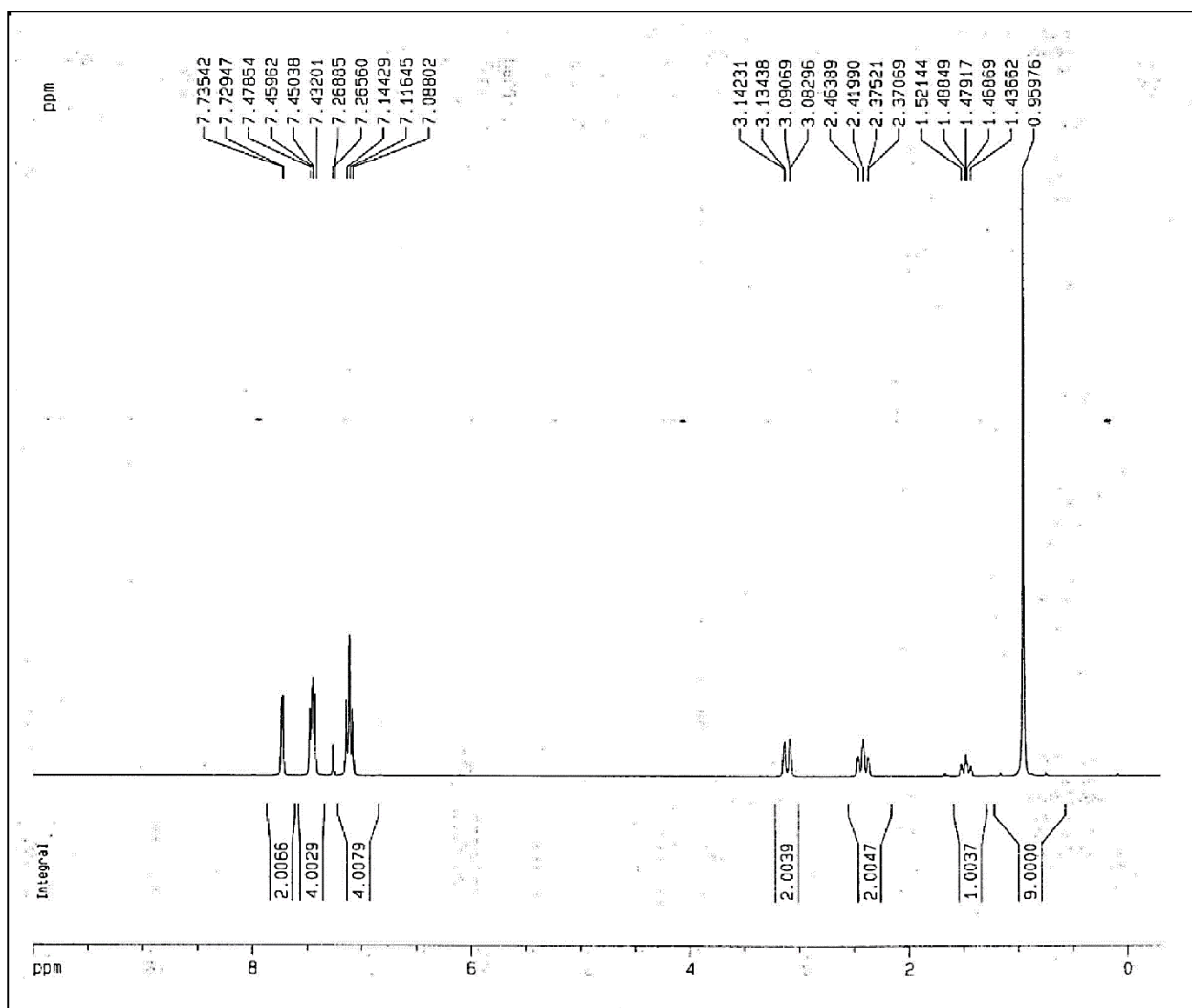


Fig. 2. ^1H NMR of 2,6-bis(4-fluorobenzylidene)-4-(tert-butyl)cyclohexanone

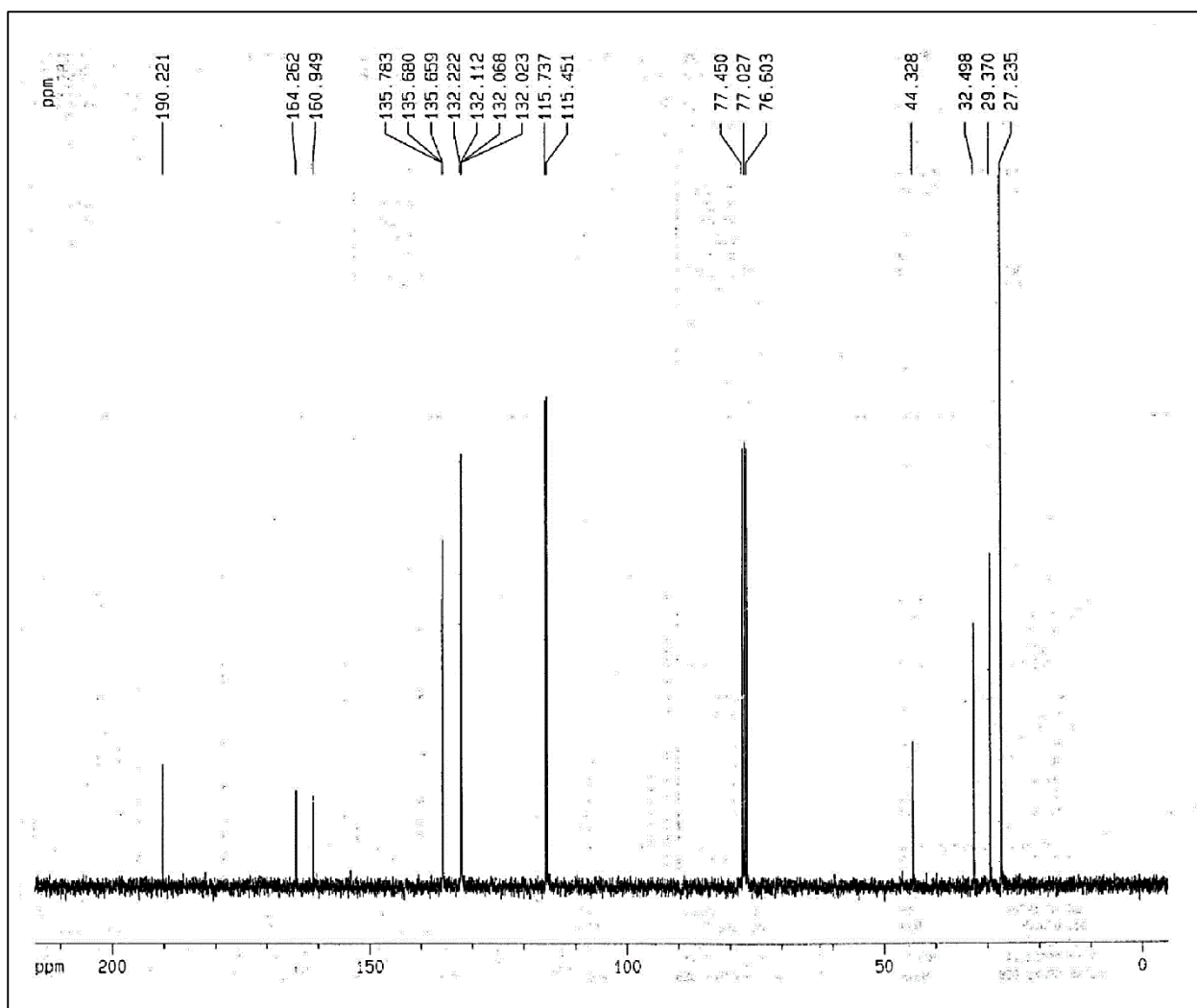


Fig. 3. ¹³C NMR of 2,6-bis(4-fluorobenzylidene)-4-(tert-butyl)cyclohexanone

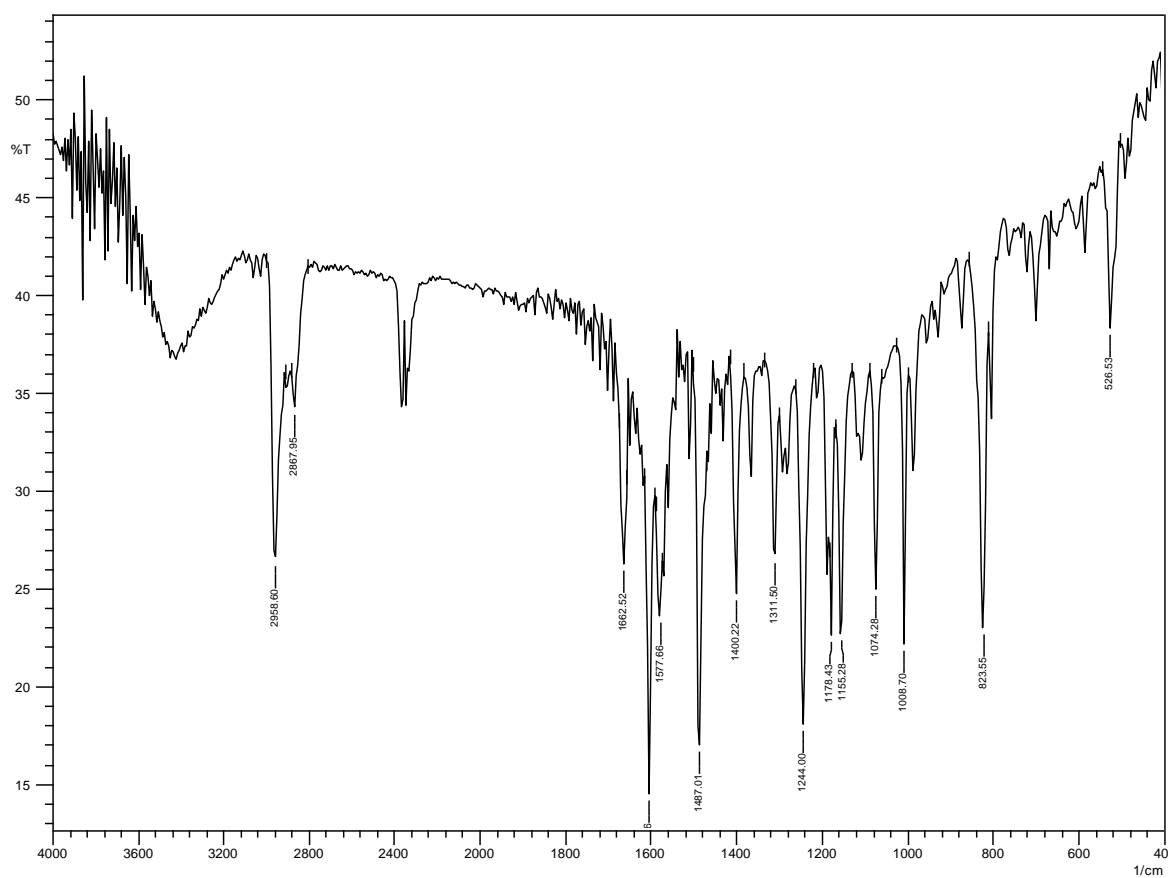


Fig. 4. FT-IR of 2,6-bis(4-bromobenzylidene)-4-(tert-butyl)cyclohexanone

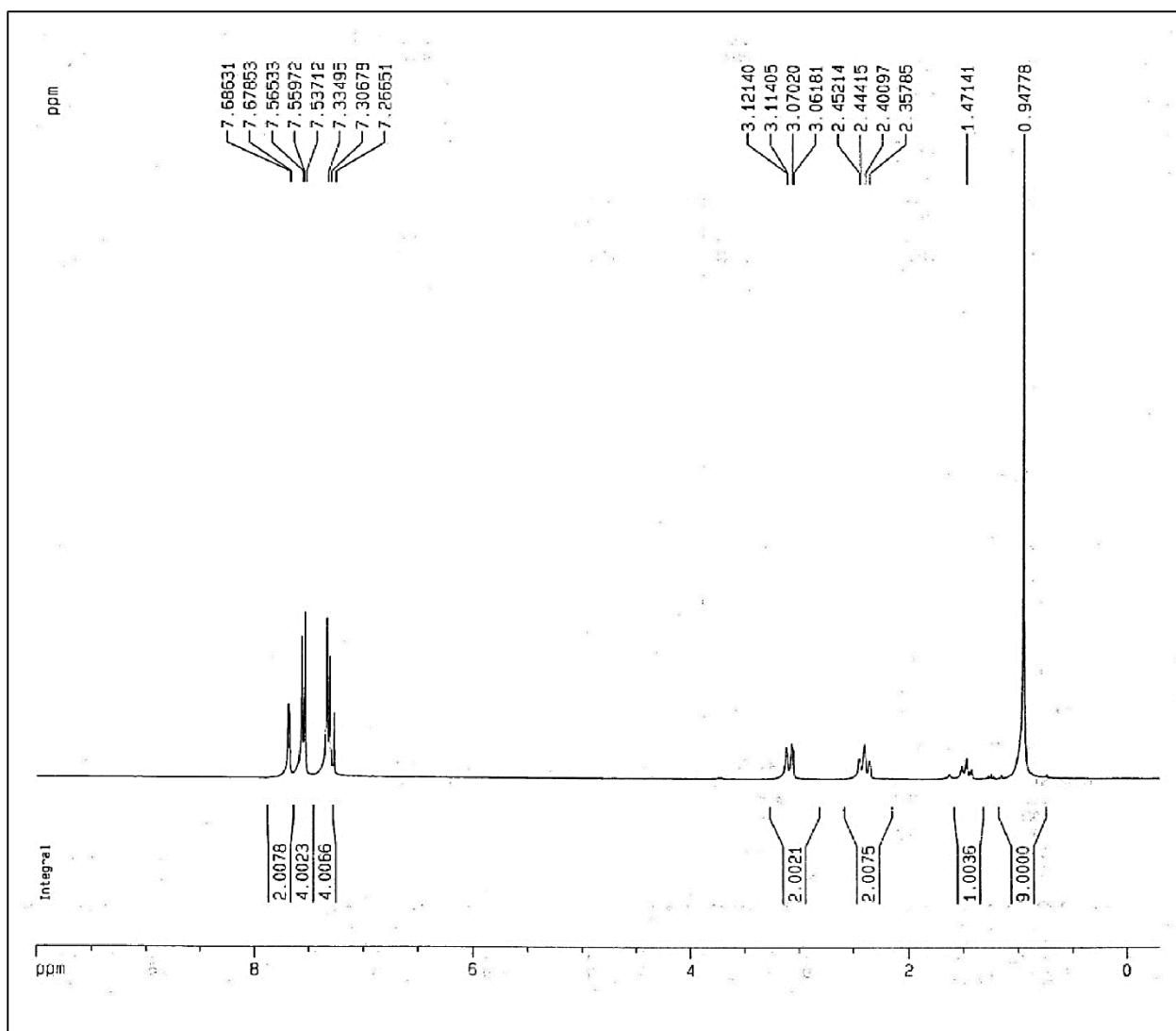


Fig. 5. ^1H NMR of 2,6-bis(4-bromobenzylidene)-4-(tert-butyl)cyclohexanone

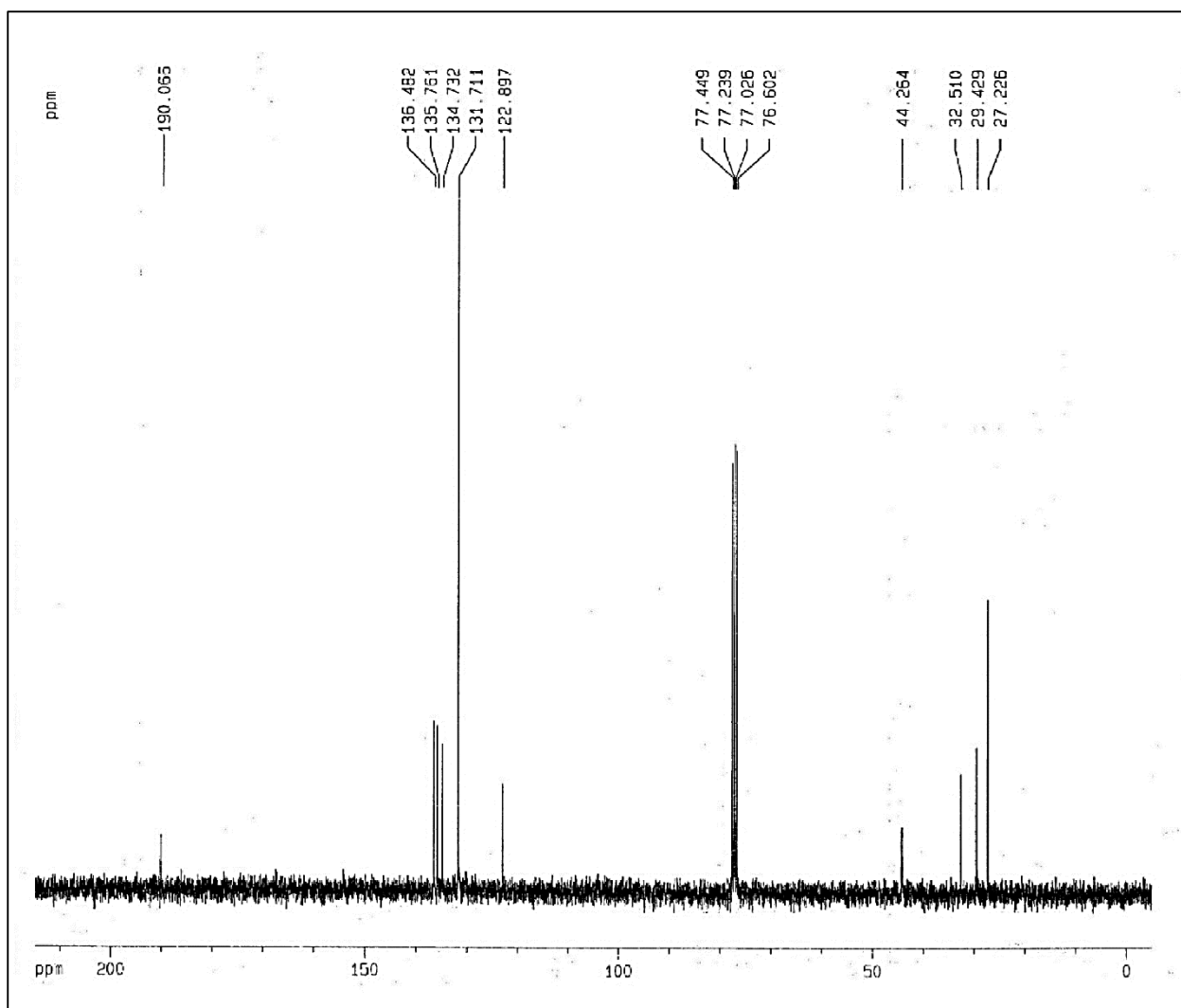


Fig. 6. ^{13}C NMR of 2,6-bis(4-bromobenzylidene)-4-(tert-butyl)cyclohexanone

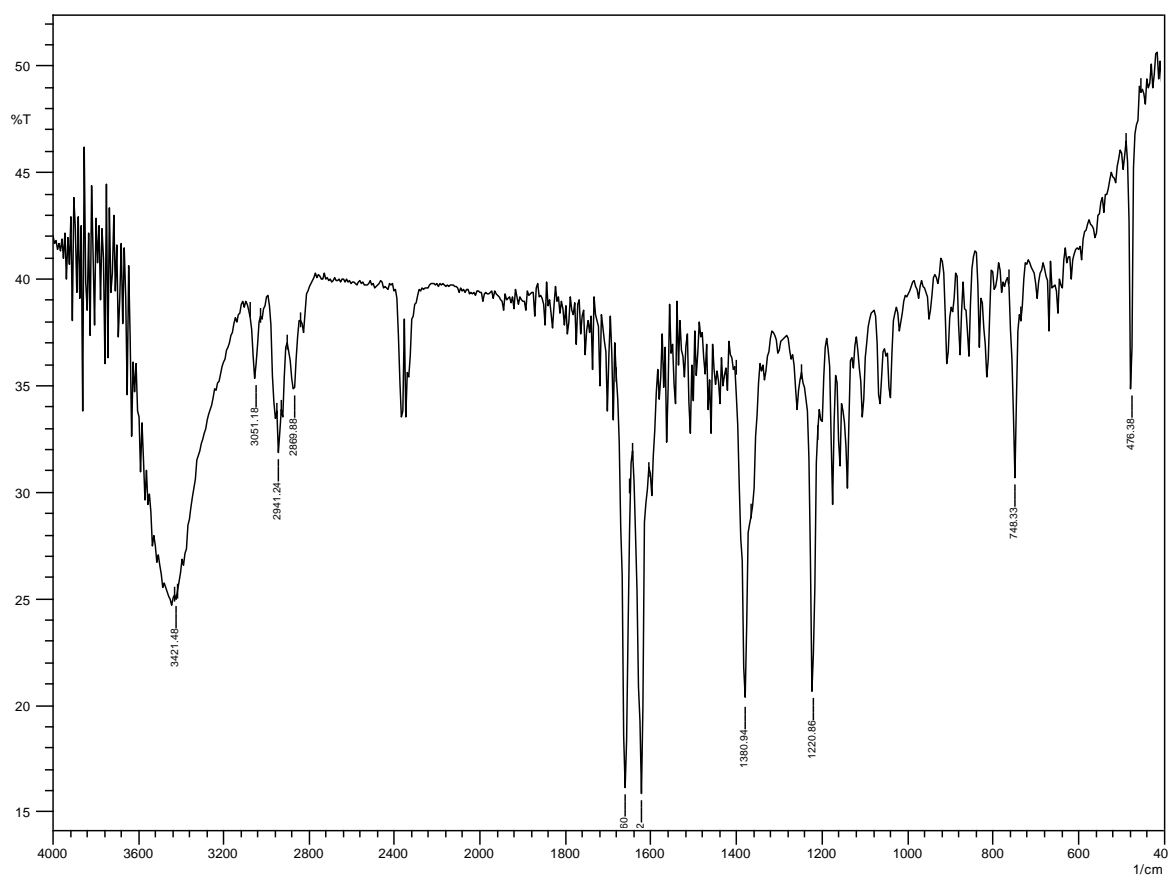


Fig. 7. FT-IR of (E)-3,3-dimethyl-9-(naphthalen-2-yl)-5-(naphthalen-2-ylmethylene)-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

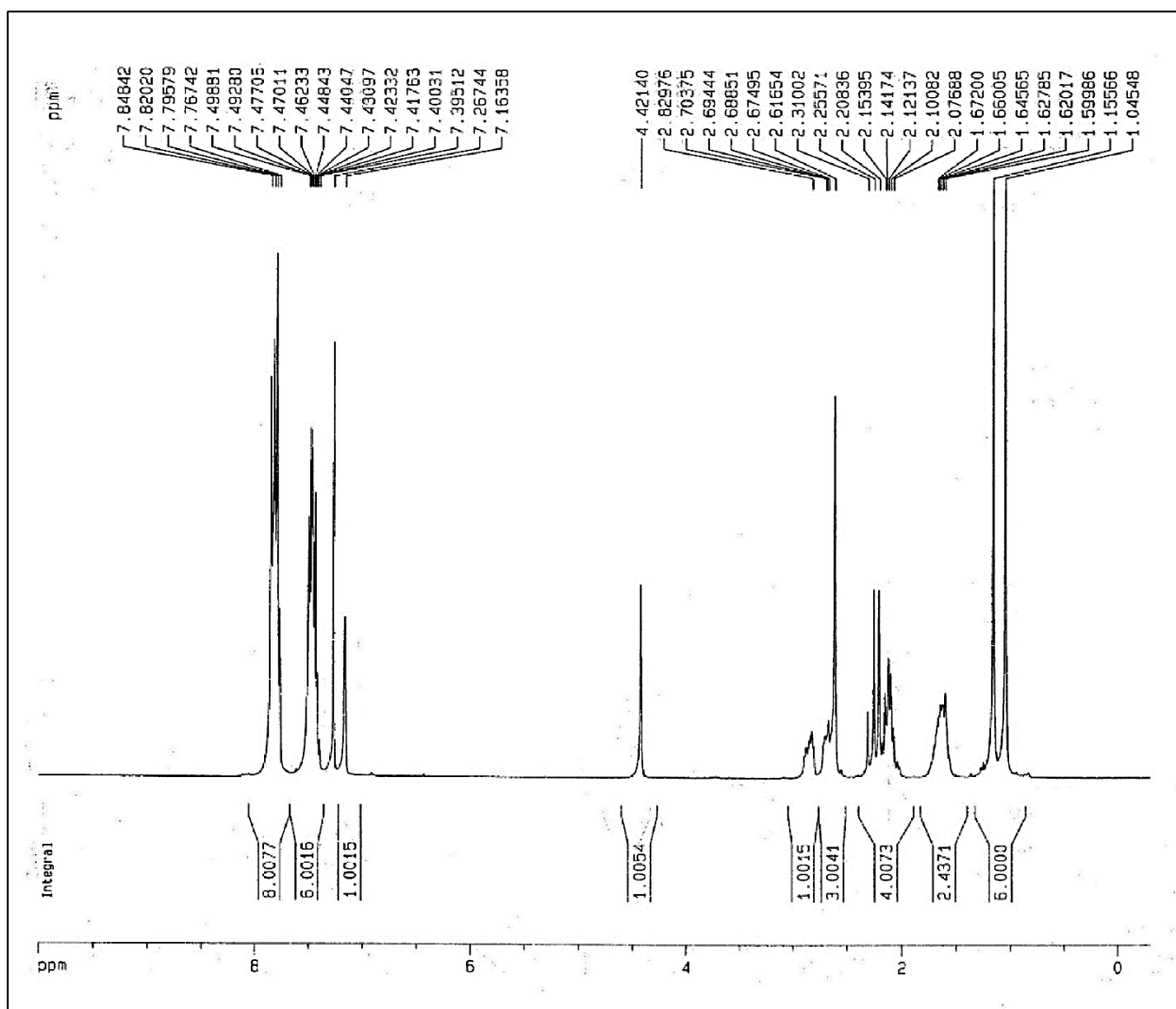


Fig. 8. ¹H NMR of (E)-3,3-dimethyl-9-(naphthalen-2-yl)-5-(naphthalen-2-ylmethylene)-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

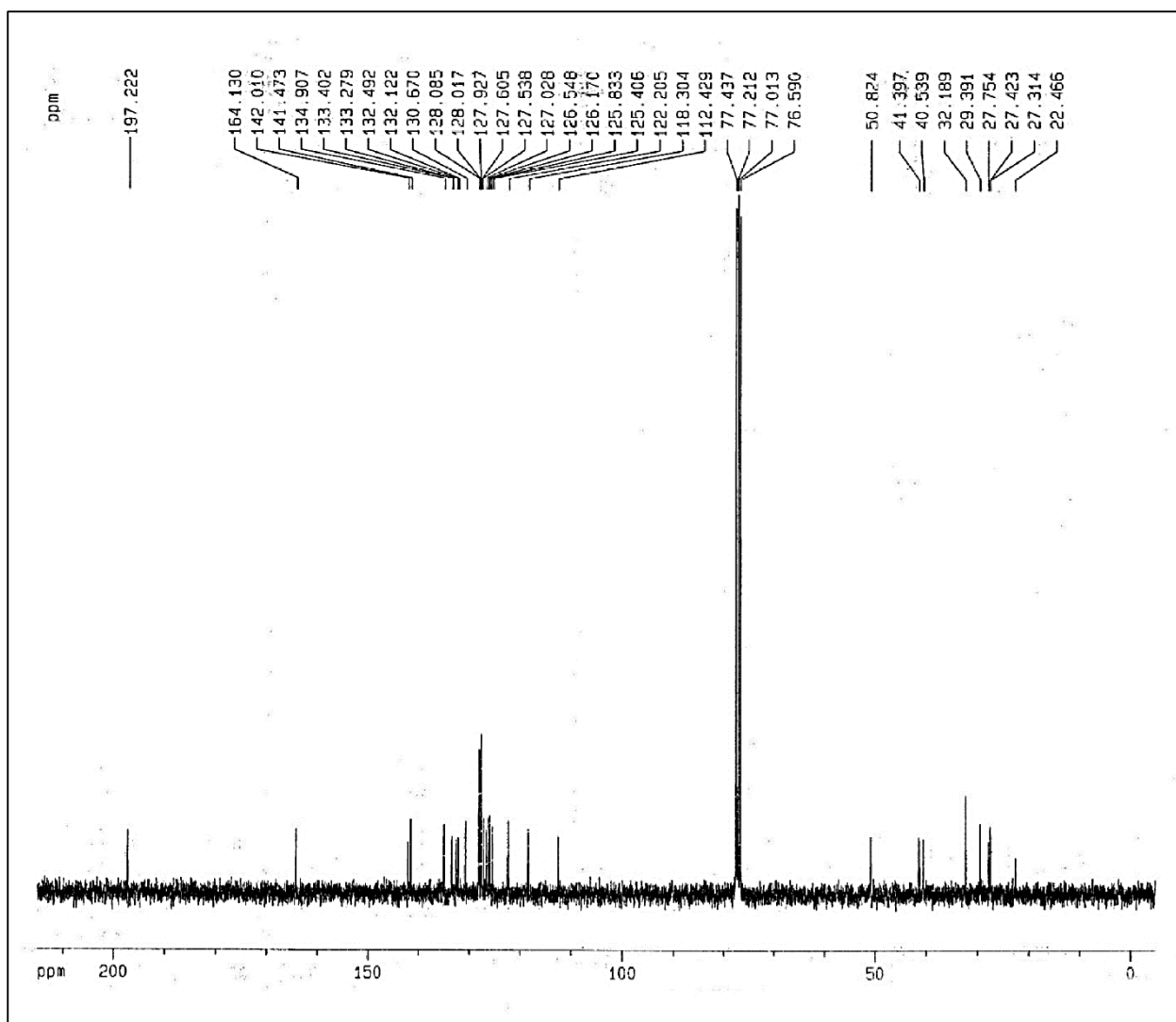


Fig. 9. ^{13}C NMR of (E)-3,3-dimethyl-9-(naphthalen-2-yl)-5-(naphthalen-2-ylmethylene)-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

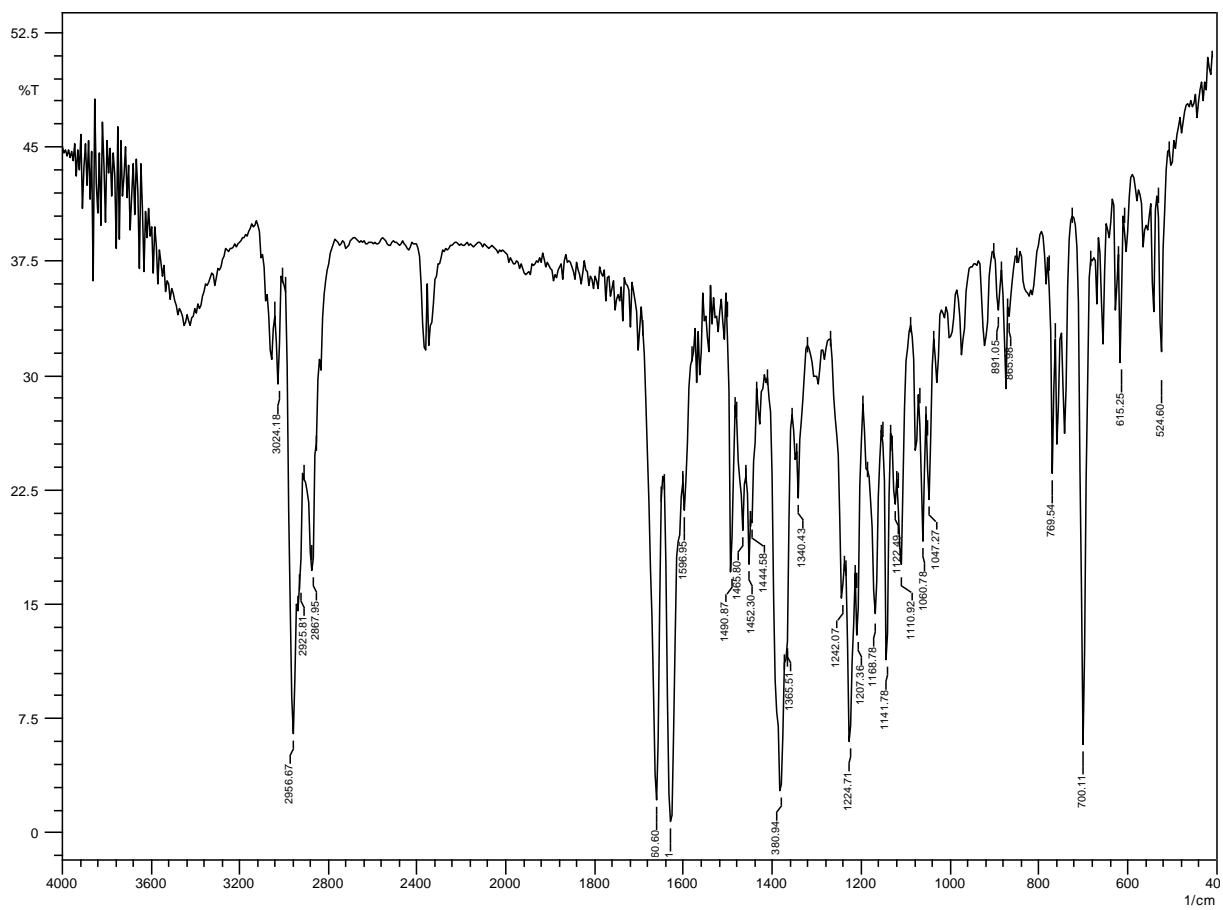


Fig. 10. FT-IR of (E)-5-benzylidene-7-(tert-butyl)-3,3-dimethyl-9-phenyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

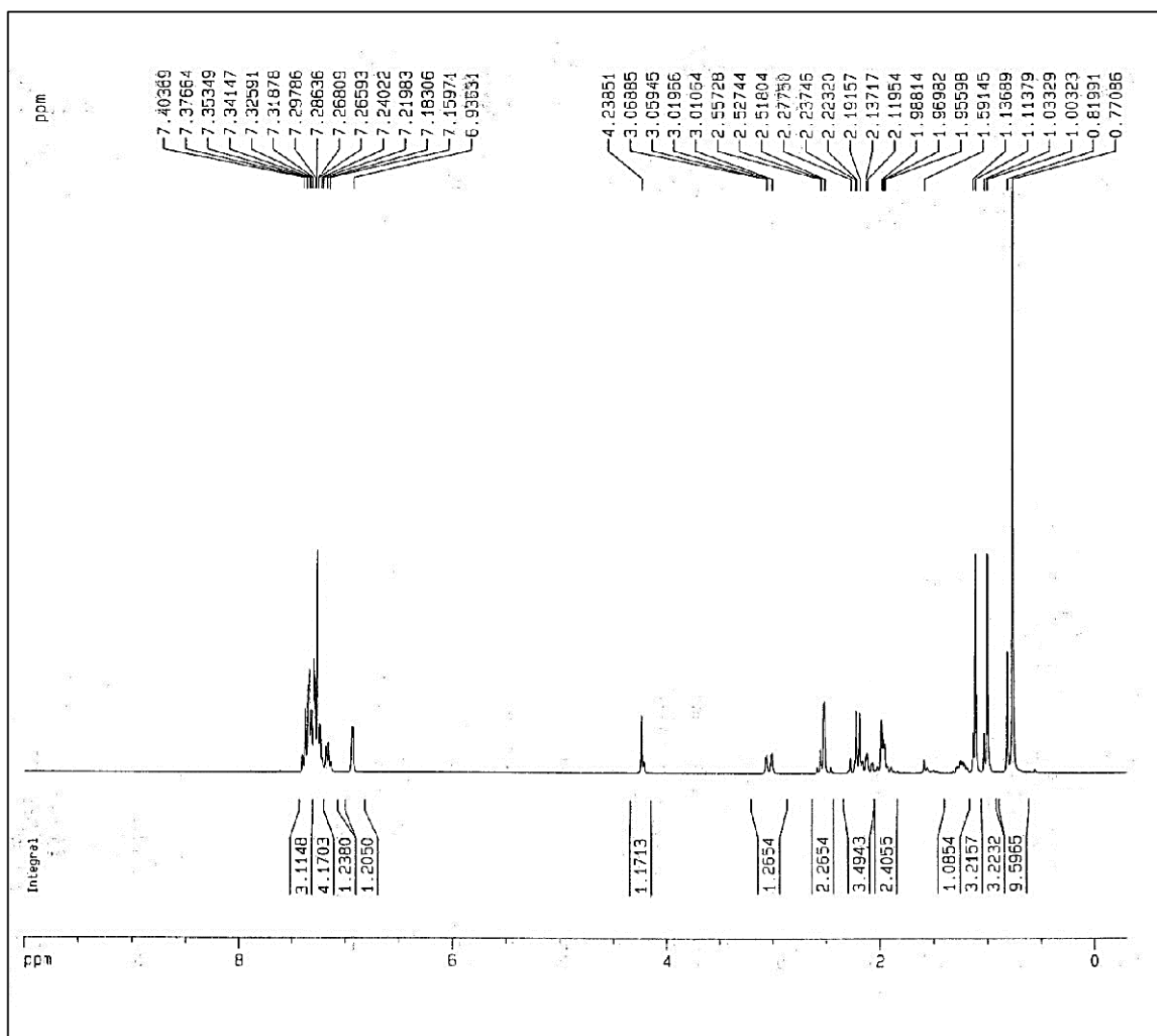


Fig. 11. ¹H NMR of (E)-5-benzylidene-7-(tert-butyl)-3,3-dimethyl-9-phenyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

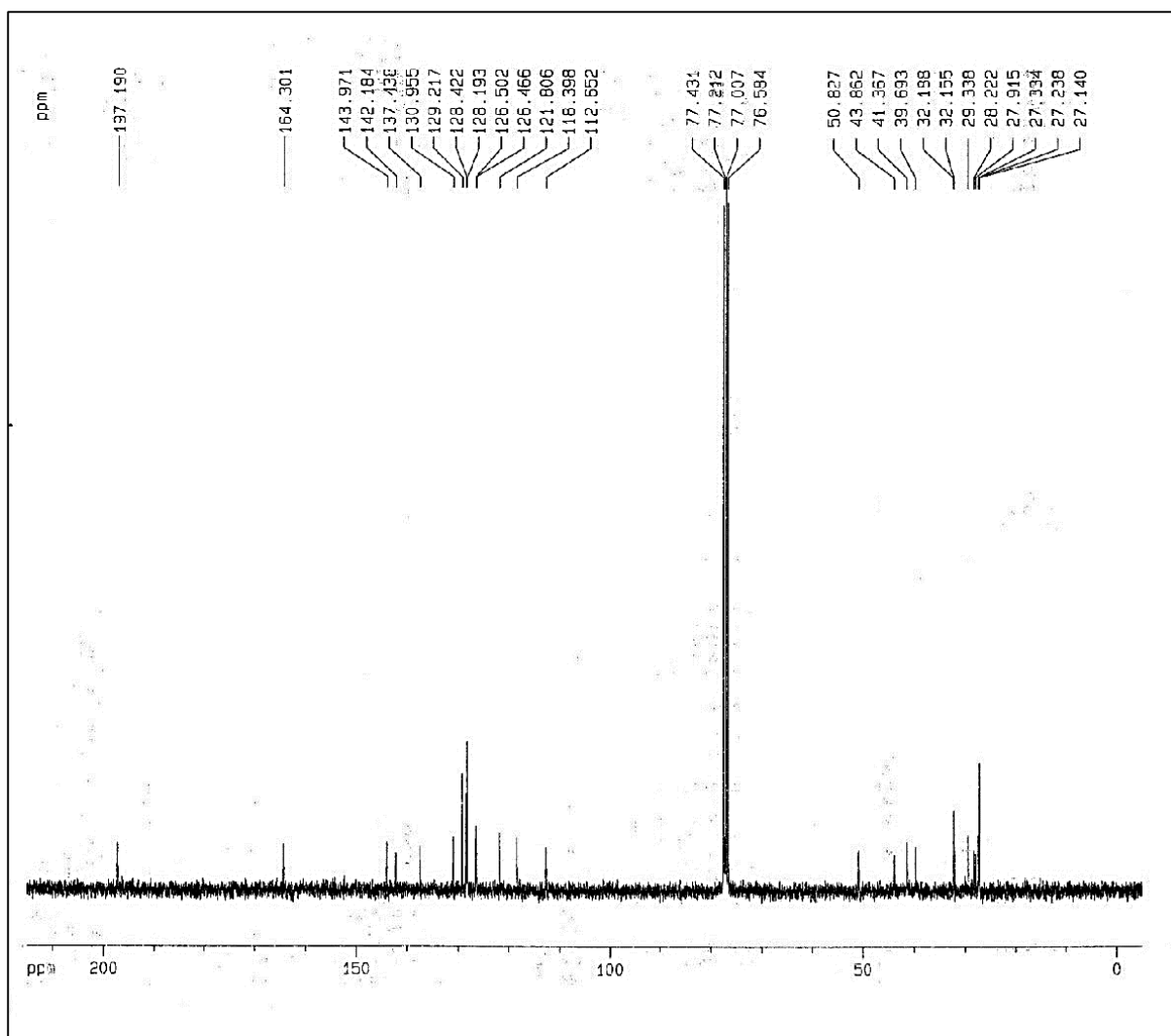


Fig. 12. ^{13}C NMR of (E)-5-benzylidene-7-(tert-butyl)-3,3-dimethyl-9-phenyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

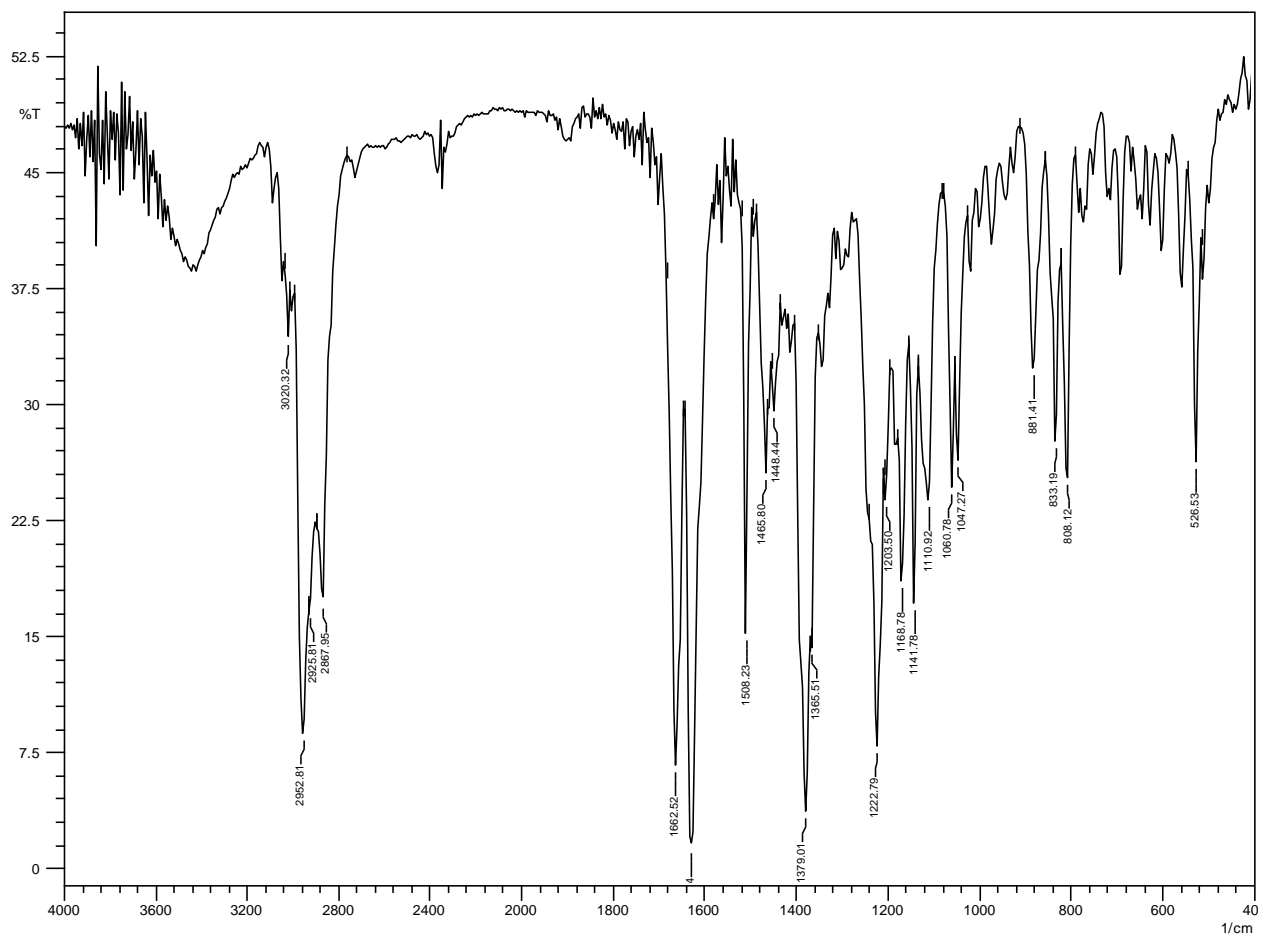


Fig. 13. FT-IR of (E)-7-(tert-butyl)-3,3-dimethyl-5-(4-methylbenzylidene)-9-(p-tolyl)-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

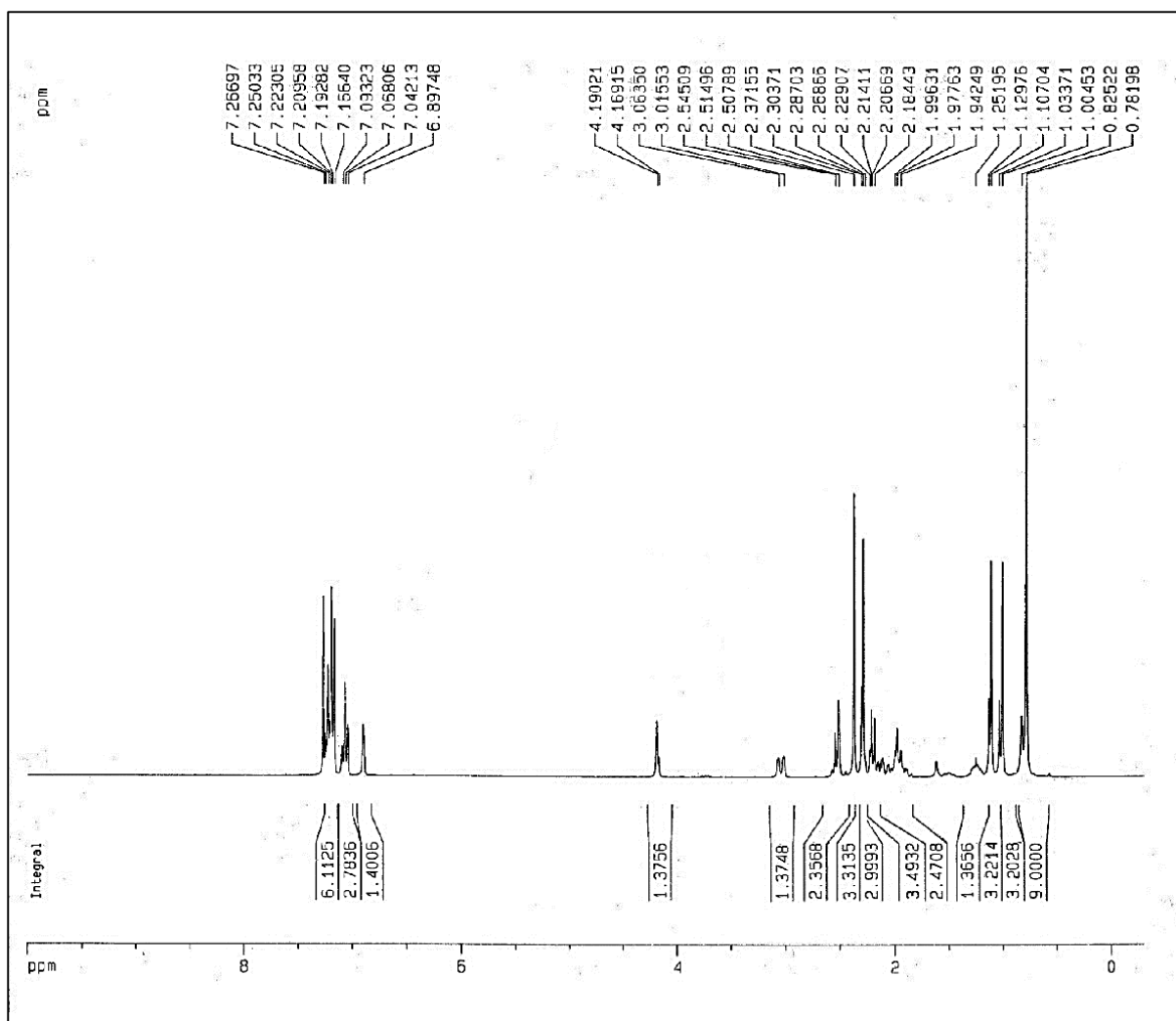


Fig. 14. ¹H NMR of (E)-7-(tert-butyl)-3,3-dimethyl-5-(4-methylbenzylidene)-9-(p-tolyl)-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

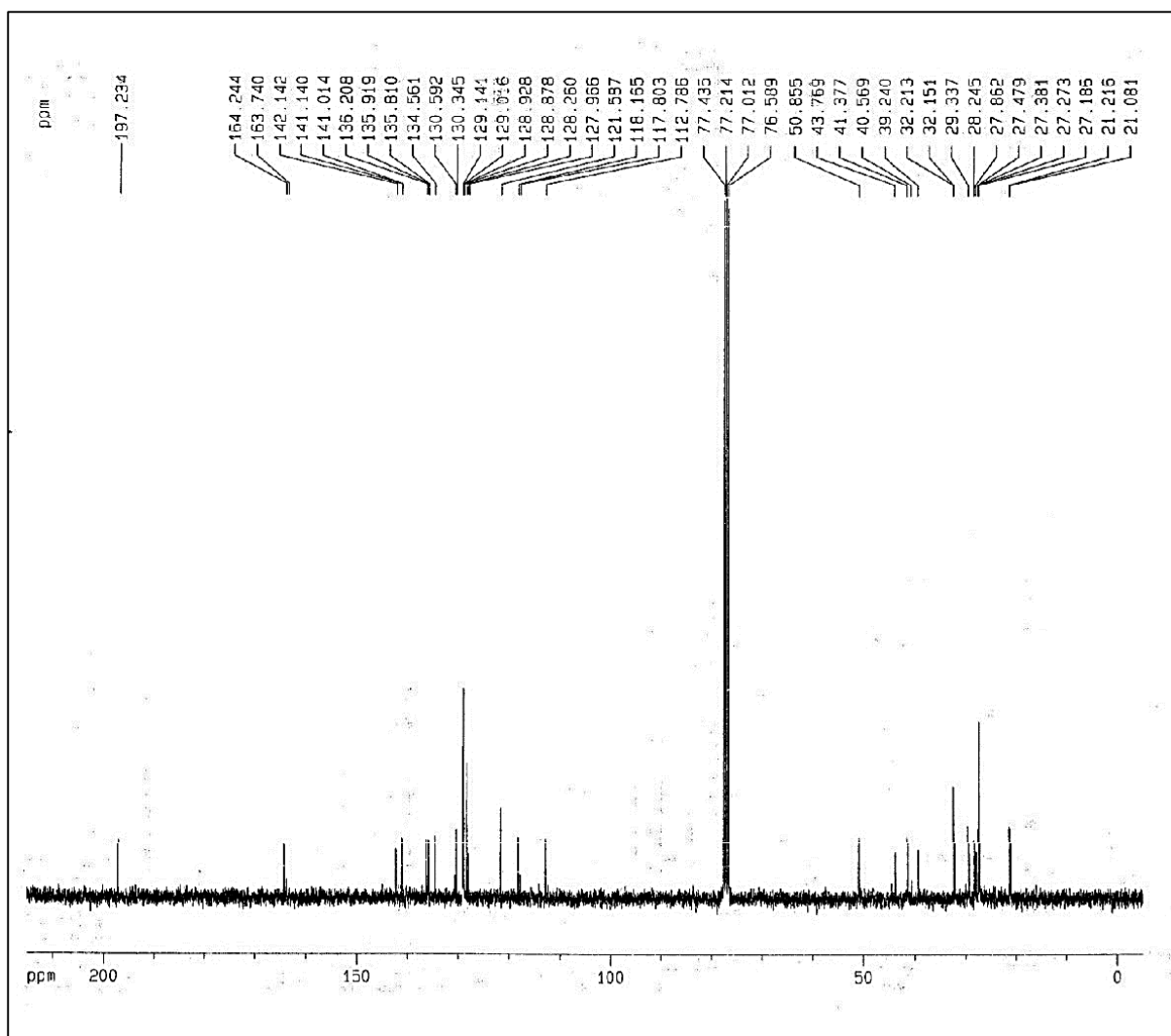


Fig. 15. ^{13}C NMR of (E)-7-(tert-butyl)-3,3-dimethyl-5-(4-methylbenzylidene)-9-(p-tolyl)-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

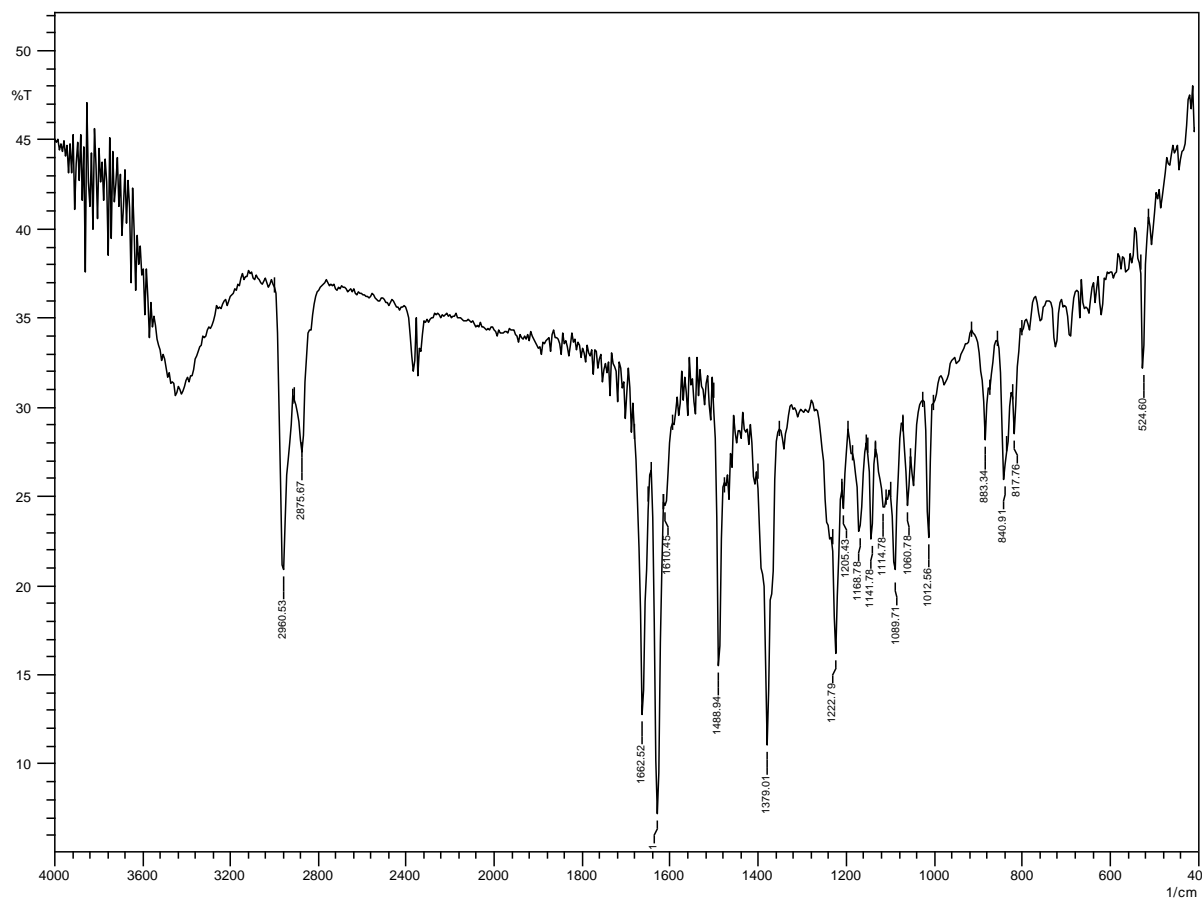


Fig. 16. FT-IR of (E)-7-(tert-butyl)-5-(4-chlorobenzylidene)-9-(4-chlorophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

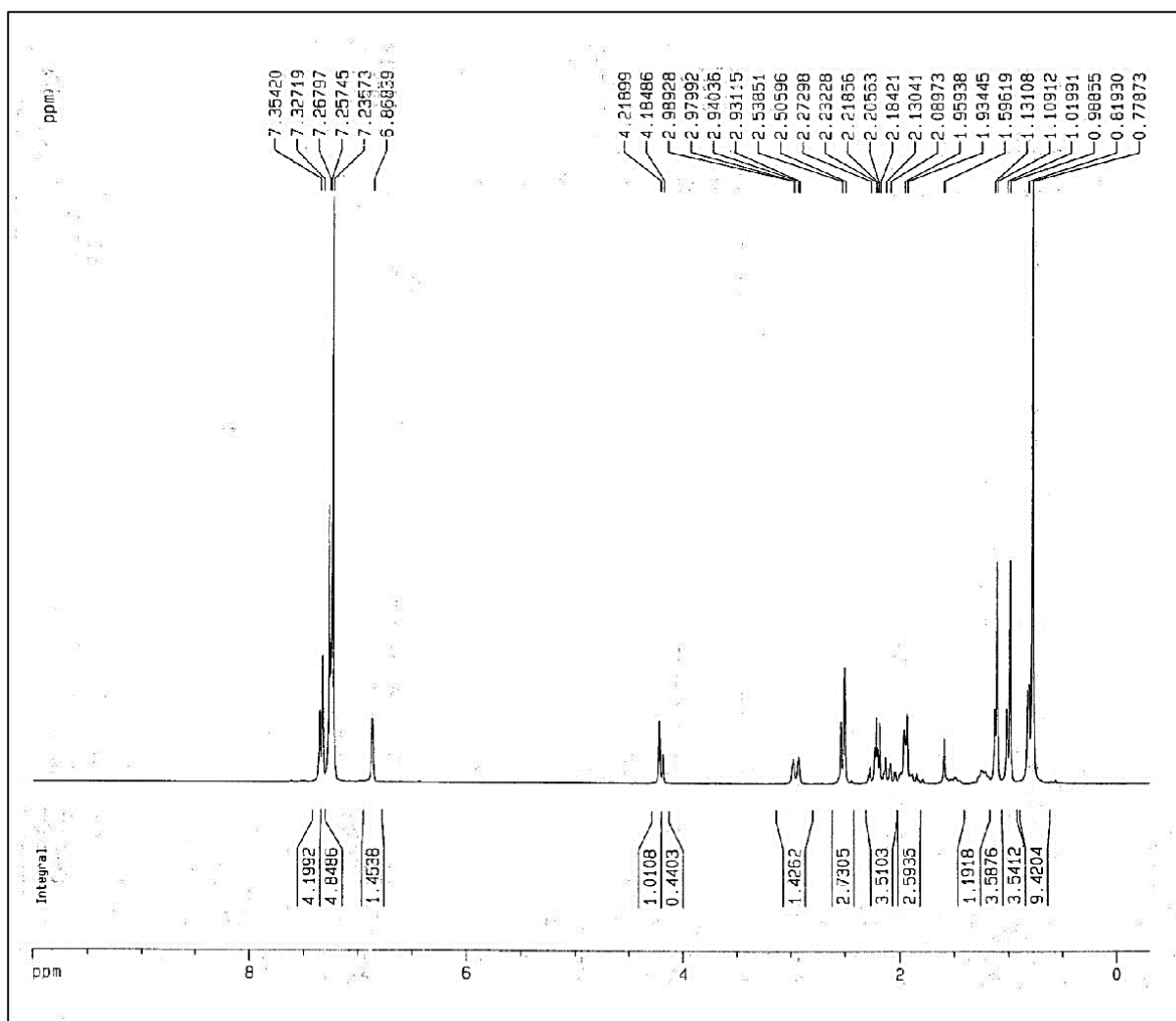


Fig. 17. ¹H NMR of (E)-7-(tert-butyl)-5-(4-chlorobenzylidene)-9-(4-chlorophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

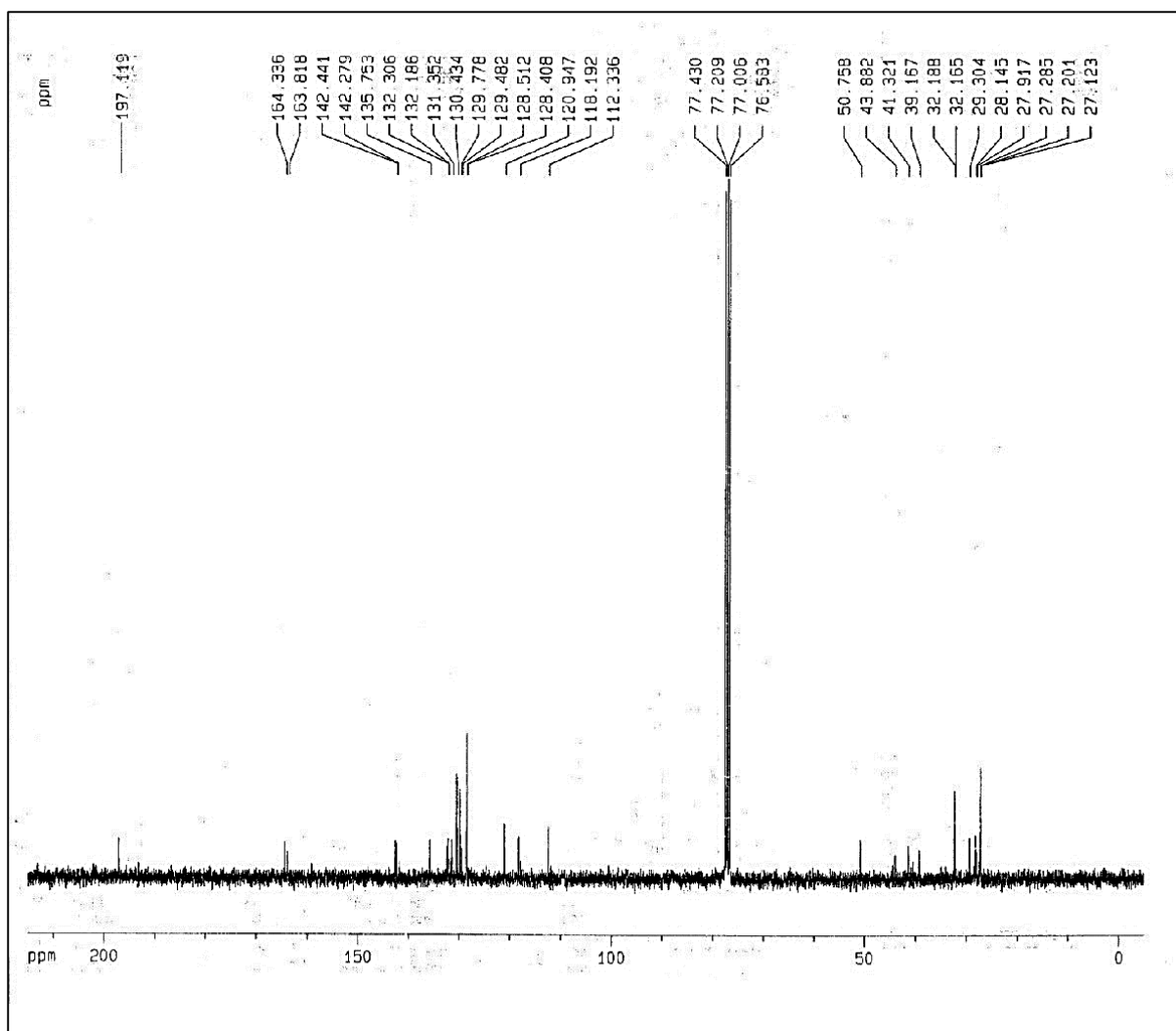


Fig. 18. ^{13}C NMR of (E)-7-(tert-butyl)-5-(4-chlorobenzylidene)-9-(4-chlorophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

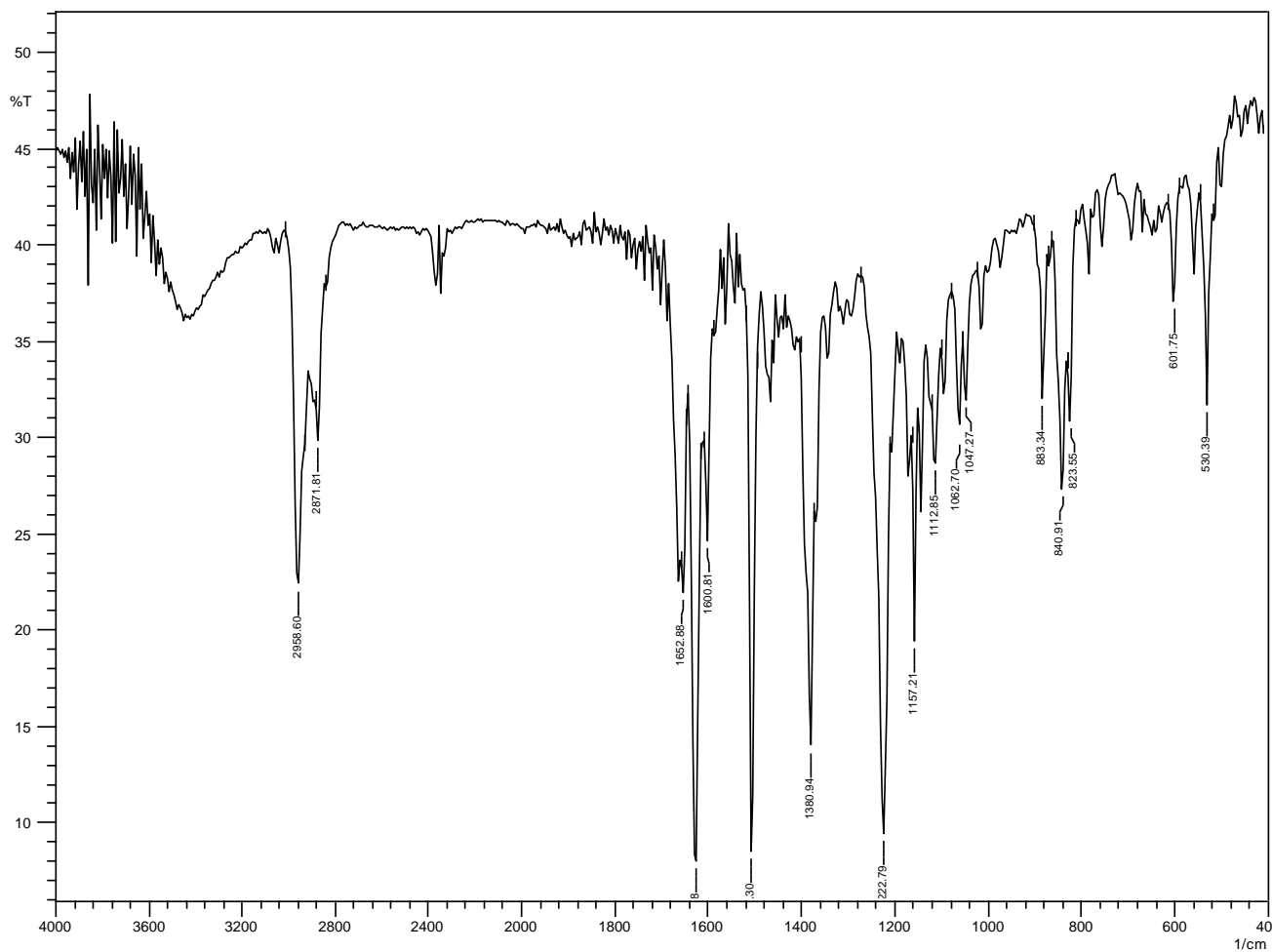


Fig. 19. FT-IR of (E)-7-(tert-butyl)-5-(4-fluorobenzylidene)-9-(4-fluorophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

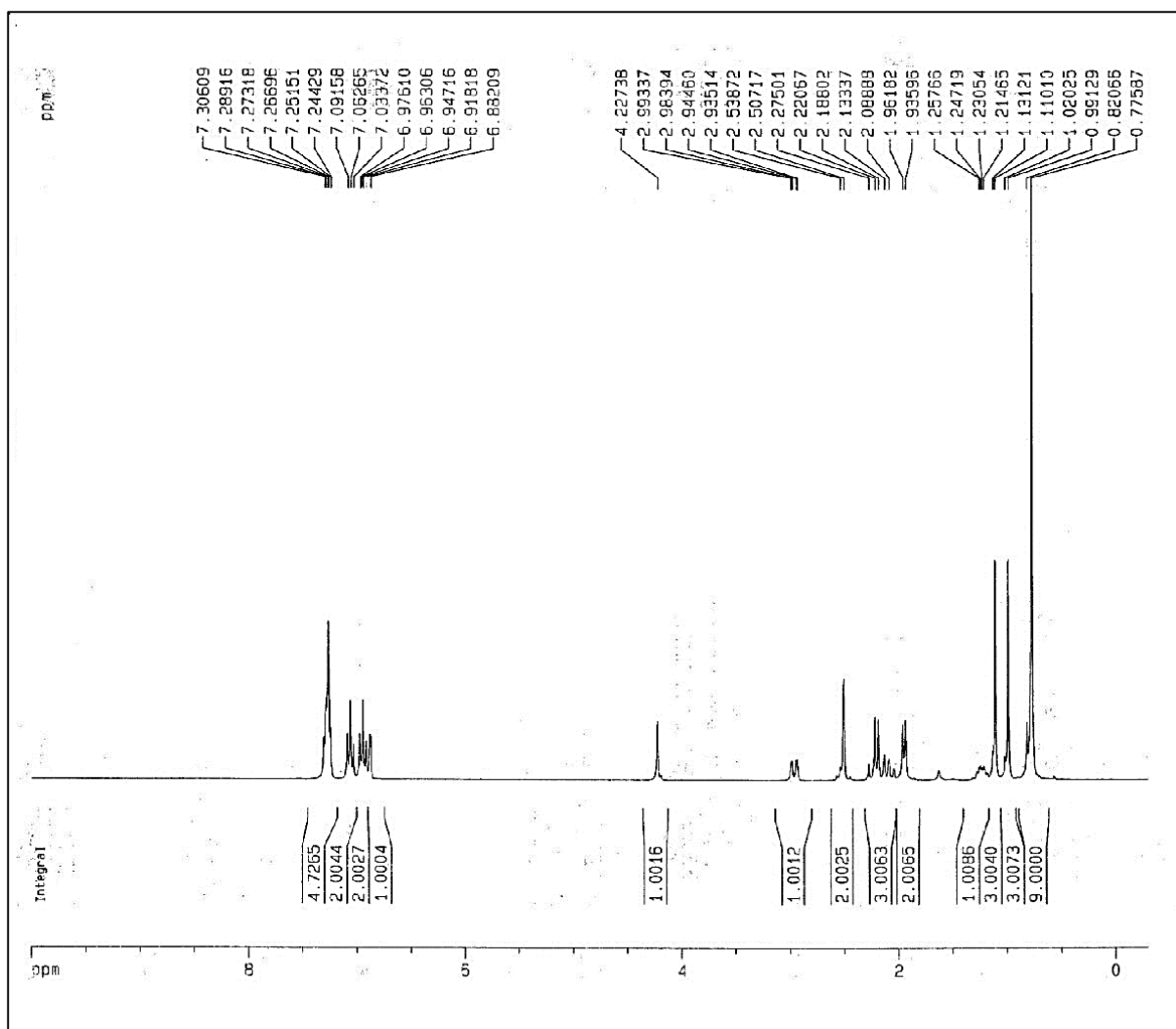


Fig. 20. ¹H NMR of (E)-7-(tert-butyl)-5-(4-fluorobenzylidene)-9-(4-fluorophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

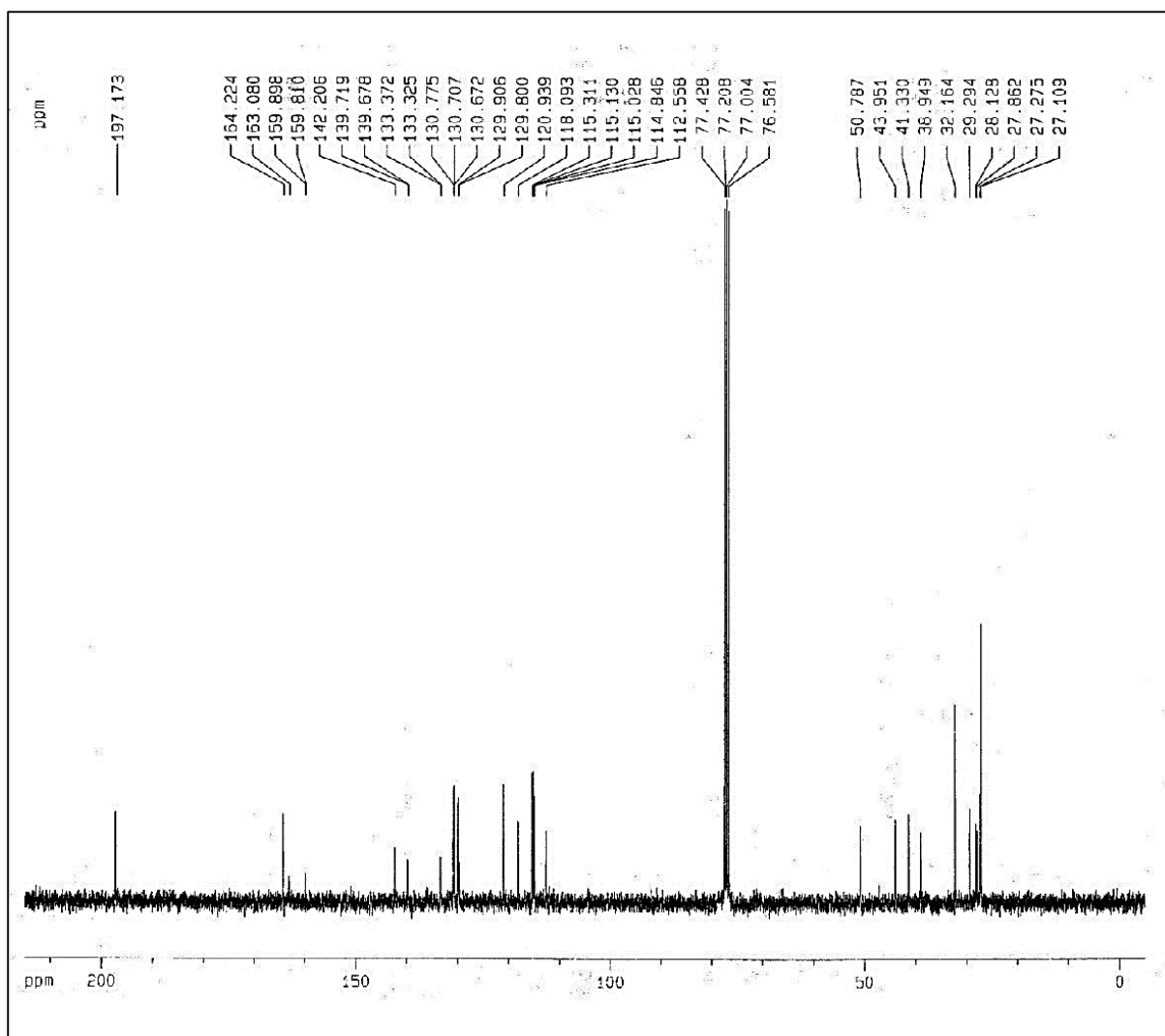


Fig. 21. ^{13}C NMR of (E)-7-(tert-butyl)-5-(4-fluorobenzylidene)-9-(4-fluorophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

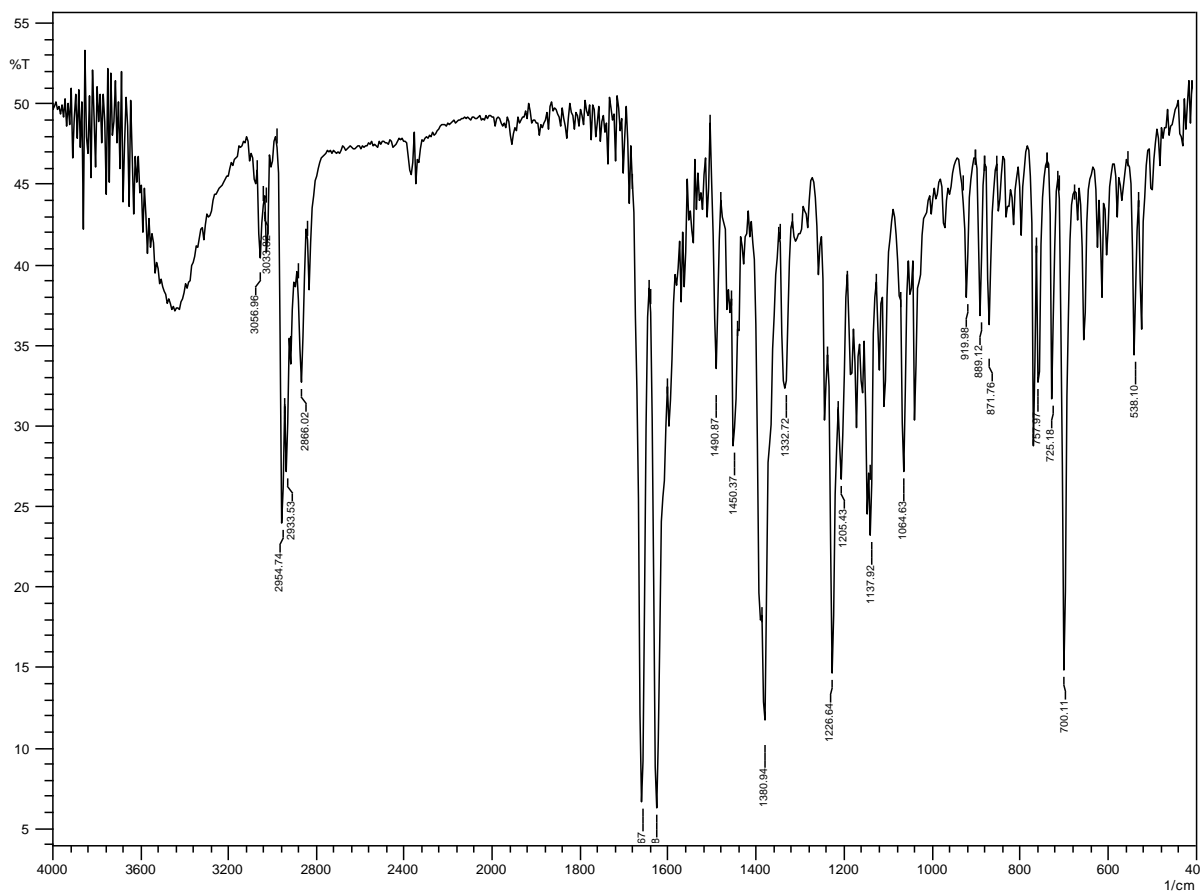


Fig. 22. FT-IR of (E)-7-(tert-butyl)-5-(4-bromobenzylidene)-9-(4-bromophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

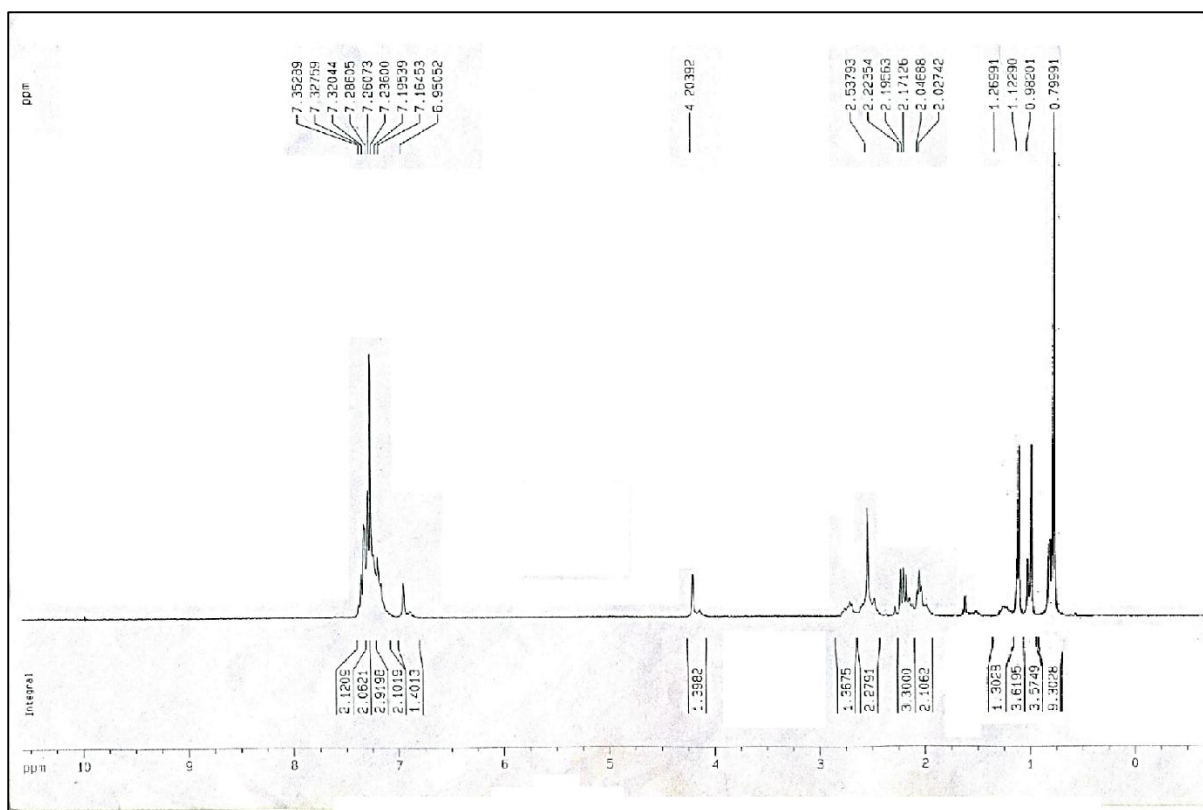


Fig. 23. ¹H NMR of (E)-7-(tert-butyl)-5-(4-bromobenzylidene)-9-(4-bromophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one

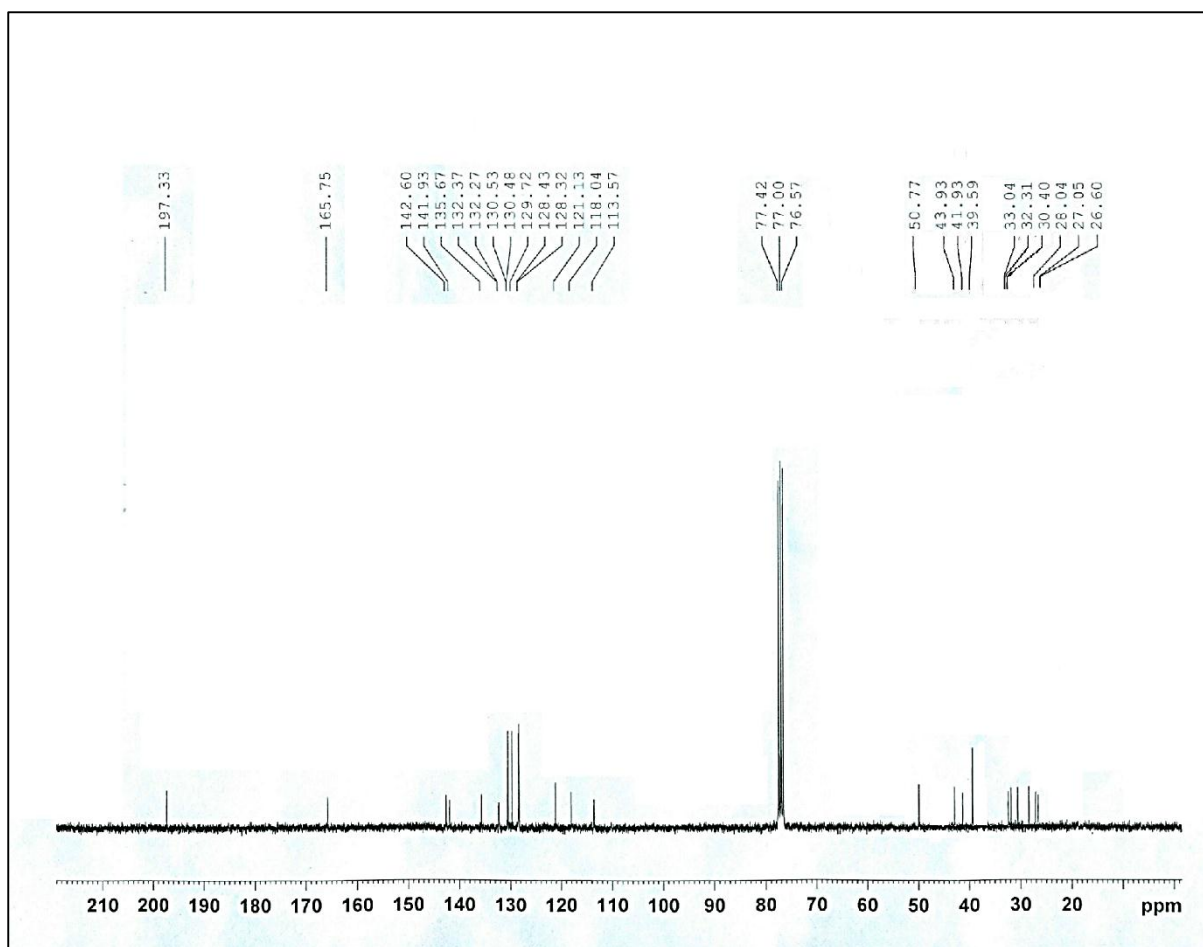


Fig. 24. ^{13}C NMR of (E)-7-(tert-butyl)-5-(4-bromobenzylidene)-9-(4-bromophenyl)-3,3-dimethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-1-one