J. Braz. Chem. Soc., Vol. 26, No. 5, S1-S25, 2015.
Printed in Brazil - ©2015 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Supplementary Information

Microwave-Assisted Heck Arylations of Non-Activated *N*-Acyl-3-pyrrolines with Arenediazonium Tetrafluoroborates

Fernanda G. Finelli, Marla N. Godoi and Carlos R. D. Correia*

Organic Chemistry Department, Institute of Chemistry, University of Campinas (Unicamp), PO Box 6154, 13087-971 Campinas-SP, Brazil

All reagents were obtained from commercial sources at the highest available purity and were used as supplied, unless stated otherwise in the experimental procedures. Solvents were purified as described by Armarego and Perrin.[1] ^{1}H and ^{13}C nuclear magnetic resonance (NMR) data were recorded with Bruker spectrometers operating at 250, 400, 500 or 600 MHz for ^{1}H with tetramethylsilane (TMS) as internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constant (Hz). High resolution mass spectra were acquired using a tandem Waters Synapt G1 high definition mass spectrometer (HDMS) (Manchester, UK) equipped with an electrospray ionization (ESI) source in positive ion mode, and a Waters Micromass GCT Premier high resolution time-of-flight (TOF) gas chromatography-mass spectrometer (GC-MS) (70 eV electron ionization, 100 μA trap current). Infrared (IR) spectra were obtained on a Thermo-Nicolet IR-200 spectrometer (Madison, WI, USA) and absorptions are reported in reciprocal centimeters. The microwave-assisted Heck-Matsuda arylations were accomplished using a CEM Discover System (Mathew, NC, USA) in heavy-walled sealed tubes with the temperature monitored by a calibrated infrared control.

Typical experimental procedure for the microwave-assisted Heck-Matsuda arylation of olefin **1**

To a solution of 1.5 eq of olefin **1** (114.22 mg, 0.675 mmol) in CH_3CN:H_2O (1:1) it was added $Pd(OAc)_2$ (2 mol%). After 5 minutes, 1 eq of arenediazonium salt was added to the reaction mixture and submitted to microwave (MW) irradiation at 60 °C and power of 100 W for 15 min. Upon completion, the mixture was cooled at r.t., diluted with AcOEt, and washed with saturated $NaHCO_3$ and NaCl solutions. The organic layers were separated, combined, and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated under vacuum. To a solution of the crude material in previously dried CH_2Cl_2 was added 1.2 eq of pyridinium chlorochromate (PCC) (174.60 mg, 0.810 mmol). After 4 h under stirring at r.t. the crude material was filtered through a plug of silica gel and washed with AcOEt. This material was evaporated and purified by flash chromatography on silica gel (AcOEt/Hex, 2:3).

tert-Butyl 4-(3,4-dimethoxyphenyl)-2-oxopyrrolidine-1-carboxylate (**3**) (Table 1, entry 1): m.p. 110-111 ºC; IR (KBr) ν_{max}/cm^{-1} 2958, 2927, 1784, 1749, 1714, 1520, 1315, 1259, 1153, 1026, 854, 777; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (s, 9H), 2.69 (dd, 1H, *J* 9.9, 17.2 Hz), 2.88 (dd, 1H, *J* 8.4, 17.2 Hz), 3.51 (q, 1H), 3.66 (dd, 1H, *J* 8.6, 10.8 Hz), 3.87 (s, 3H), 3.88 (s, 3H), 4.14 (dd, 1H, *J* 8.1, 11.0 Hz), 6.73-6.86 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.9, 36.1, 40.4, 53.2, 55.9, 83.0, 110.0, 111.5, 118.7, 133.0, 148.4, 149.3, 150.0, 173.1; HRMS (ESI(+)-MS) *m/z* calcd. for $C_{17}H_{23}NO_5Na$: 344.1474; found: 344.1550.

tert-Butyl 4-(4-chlorophenyl)-2-oxopyrrolidine-1-carboxylate (**4**) (Table 1, entry 2): m.p. 98 ºC; IR (KBr) ν_{max}/cm^{-1} 2979, 2931, 1788, 1749, 1714, 1495, 1367, 1315, 1257, 1153, 1107, 1014, 831, 777; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54 (s, 9H), 2.67 (dd, 1H, *J* 9.5, 17.2 Hz), 2.90 (dd, 1H, *J* 8.4, 17.2 Hz), 3.52 (q, 1H), 3.65 (dd, 1H, *J* 8.3, 11.0 Hz), 4.15 (dd, 1H, *J* 7.9, 10.8 Hz), 7.18 (d, 2H, *J* 8.8 Hz), 7.33 (d, 2H, *J* 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.0, 35.9, 40.2, 52.9, 83.3, 128.1, 129.2, 133.3, 139.1, 149.8, 172.6; HRMS (ESI(+)-MS) *m/z* calcd. for $C_{15}H_{18}ClNO_3Na$: 318.0873; found: 318.0868.

tert-Butyl 4-(4-methoxyphenyl)-2-oxopyrrolidine-1-carboxylate (**5**) (Table 1, entry 3): m.p. 92-96 ºC; IR (KBr) ν_{max}/cm^{-1} 2978, 2933, 1785, 1750, 1714, 1516, 1317, 1252, 1153, 1035, 833, 777; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52 (s, 9H), 2.65 (dd, 1H, *J* 9.9, 17.2 Hz), 2.85 (dd, 1H, *J* 8.4,

*e-mail: roque@iqm.unicamp.br

17.2 Hz), 3.46 (q, 1H), 3.63 (dd, 1H, *J* 8.6, 10.9 Hz), 3.78 (s, 3H), 4.11 (dd, 1H, *J* 7.9, 10.8 Hz), 6.86 (d, 2H, *J* 8.8 Hz), 7.15 (d, 2H, *J* 8.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.9, 35.7, 40.4, 53.3, 55.2, 82.9, 114.3, 127.7, 132.4, 149.8, 158.8, 173.1; HRMS (ESI(+)-MS) *m/z* calcd. for $C_{16}H_{21}NO_4Na$: 314.1368; found: 314.1418.

tert-Butyl 4-(4-nitrophenyl)-2-oxopyrrolidine-1-carboxylate (**6**) (Table 1, entry 4): m.p. 105-106 ºC; IR (KBr) ν_{max}/cm^{-1} 2979, 2931, 1788, 1749, 1714, 1495, 1367, 1315, 1255, 1153, 1107, 1014, 831, 777; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (s, 9H), 2.72 (dd, 1H, *J* 9.4, 17.2 Hz), 2.98 (dd, 1H, *J* 8.1, 17.2 Hz), 3.70 (m, 2H), 4.22 (dd, 1H, *J* 7.6, 10.1 Hz), 7.44 (d, 2H, *J* 8.8 Hz), 8.23 (d, 2H, *J* 8.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.9, 36.1, 39.9, 52.4, 83.5, 124.2, 127.7, 147.3, 148.1, 149.6, 171.8; HRMS (ESI(+)-MS) *m/z* calcd. for $C_{15}H_{18}N_2O_5Na$: 329.1113; found: 329.1075.

tert-Butyl 4-(naphthalen-2-yl)-2-oxopyrrolidine-1-carboxylate (**7**) (Table 1, entry 5): m.p. 122-123 ºC; IR (KBr) ν_{max}/cm^{-1} 3053, 2978, 1784, 1749, 1712, 1367, 1317, 1151, 856, 748; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (s, 9H), 2.84 (dd, 1H, *J* 9.5, 17.2 Hz), 3.0 (dd, 1H, *J* 8.4, 17.2 Hz), 3.71 (q, 1H), 3.81 (dd, 1H, *J* 8.1, 10.6 Hz), 4.25 (dd, 1H, *J* 8.0, 10.5 Hz), 7.37 (dd, 1H, *J* 1.8, 8.4 Hz), 7.50 (dd, 2H, *J* 2.2, 9.5 Hz), 7.68 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.0, 36.5, 40.2, 53.0, 83.1, 124.7, 125.4, 126.1, 126.5, 127.7, 128.9, 132.6, 133.4, 137.9, 149.9, 173.0; EM (70 eV, *m/z*, relative abundance) 311 (26), 238 (6), 211 (25), 154 (100), 57 (70).

Typical experimental procedure for the microwave-assisted Heck-Matsuda arylation of olefin **2**

To a solution of 1.0 eq of olefin **2** (50.0 mg, 0.27 mmol) in CH_3OH (1.0 mL) it was added $Pd(OAc)_2$ (10 mol%) followed by the addition of 2 eq of the corresponding arenediazonium salt. The reaction mixture under stirring was submitted to MW irradiation at 100 °C and power of 100 W for 12-30 min. Upon completion, the reaction mixture was cooled at r.t., diluted with EtOAc, and washed with saturated $NaHCO_3$ and NaCl solutions. The organic layers were separated, combined, and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo* and the crude material purified by flash chromatography on silica gel.

Dimethyl 2-methoxy-4-(4-methoxyphenyl)pyrrolidine-1,2-dicarboxylate (**8**) (Table 3, entry 1): IR (KBr) ν_{max}/cm^{-1} 2953, 2899, 2837, 1758, 1710, 1612, 1515, 1444, 1364, 1249, 1199, 1180, 1032, 831; ^{1}H NMR (300 MHz, $CDCl_3$)[a] δ 2.27-2.54 (m, 2H), 3.45-4.08 (m, 15H, overlap of several signals), 6.86 (d, 2H, *J* 8.4 Hz), 7.21 (d, 2H, *J* 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 39,67, 40.44, 46.02, 52.73, 52.99, 54.63, 55.29, 92.99, 114.13, 128.13, 131.41, 158.75, 170.07; HRMS (ESI(+)-MS) *m/z* calcd. for $C_{16}H_{21}NO_6Na$: 346.1267; found: 346.1096. [a]Mixture of rotamers and diastereoisomers.

Dimethyl 2-methoxy-4-(2-methoxyphenyl)pyrrolidine-1,2-dicarboxylate (**9**) (Table 3, entry 2): IR (KBr) ν_{max}/cm^{-1} 2999, 2954, 2904, 1756, 1711, 1446, 1368, 1247, 1201, 1114, 1083, 1052, 1025, 754; ^{1}H NMR (300 MHz, $CDCl_3$)[a] δ 2.30-2.42 (m, 2H), 3.40-4.04 (m, 15H, several signals overlapping), 6.86-6.96 (m, 2H), 7.09-7.19 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$)[a] δ 34.85, 35.41, 43.41, 43.61, 51.96, 52.70. 52.85, 53.24, 55.20, 92.72, 110.36, 120.49, 126.78, 127.36, 128.06, 155.47, 157.64, 170.31. [a]Mixture of rotamers and diastereoisomers.

Dimethyl 2-hydroxy-4-(2-methoxyphenyl)pyrrolidine-1,2-dicarboxylate (**10**) (Table 2, entry 10): IR (film) ν_{max}/cm^{-1} 3479, 2955, 2896, 2838, 1750, 1702, 1601, 1495, 1451, 1384, 1244, 1211, 1194, 1105, 1053, 1025, 990, 777, 754; ^{1}H NMR (250 MHz, $CDCl_3$)[a] δ 2.33-2.57 (m, 2H), 3.42-4.12 (m, 12 H, several signals overlapping), 6.86-6.96 (m, 2H), 7.16-7.28 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$)[a] δ 34.91, 35.48, 43.50, 43.72, 52.03, 52.32, 52.77, 52.84, 52.94, 53.31, 55.27, 92.81, 110.43, 120.57, 126.88, 127.88, 127,47, 128.12, 155.55, 157.73, 170.40; HRMS (ESI(+)-MS) *m/z* calcd. for $C_{15}H_{19}NO_6Na$: 332.1110; found: 332.1104. [a]Mixture of rotamers and diastereoisomers.

Dimethyl 4-(4-fluorophenyl)-2-methoxypyrrolidine-1,2-dicarboxylate (**11**) (Table 3, entry 3): IR (KBr) ν_{max}/cm^{-1} 2955, 1755, 1713, 1606, 1513, 1447, 1367, 1229, 1203, 1125, 1085, 837; ^{1}H NMR (300 MHz, $CDCl_3$)[a] δ 2.29-2.56 (m, 2H), 3.39-4.08 (m, 12H, several signals overlapping), 6.98-7.04 (m, 2H), 7.19-7.26 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$)[a] δ 39.67, 40.44, 45.95, 46.19, 46.30, 52.19, 52.41, 52.81, 52.90, 53.03, 53.09, 54.49, 54.99, 56.70, 92.46, 92.88, 115.46, 115.63, 115.70, 115.87, 128.60, 128.67, 128.79, 135.10, 135.13, 155.40, 160.91, 162.87, 169.91; HRMS (ESI(+)-MS) *m/z* calcd. for $C_{15}H_{18}FNO_5$: 334.1067; found: 334.1044. [a]Mixture of rotamers and diastereoisomers.

Dimethyl 4-(4-bromophenyl)-2-methoxypyrrolidine-1,2-dicarboxylate (**12**) (Table 3, entry 4): IR (KBr) ν_{max}/cm^{-1} 2988, 2953, 2843, 1758, 1713, 1491, 1446, 1368, 1202, 1125, 1078, 1051, 1010, 980, 940, 822; ^{1}H NMR

(300 MHz, $CDCl_3$)[a] δ 2.29-2.43 (m, 2H), 3.45-3.98 (m, 12H, several signals overlapping), 7.13 (d, 2H, *J* 8.5 Hz), 7.45 (d, 2H, *J* 8.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$)[a] δ 39.98, 40.62, 45.74, 45.80, 52.84, 52.93, 53.05, 54.21, 92.85, 121.0, 128.89, 131.80, 138.47, 155.37, 169.85; HRMS (ESI(+)-MS) *m/z* calcd. for $C_{14}H_{15}BrNO_4$ (M–OMe): 341.0263; found: 341.0165. [a]Mixture of rotamers and diastereoisomers.

Dimethyl 4-(3,4-dichlorophenyl)-2-methoxypyrrolidine-1,2-dicarboxylate (**13**) (Table 3, entry 5): IR (KBr) ν_{max}/cm^{-1} 3478, 3001, 2955, 1751, 1705, 1453, 1381, 1105, 930, 737; ^{1}H NMR (300 MHz, $CDCl_3$)[a] δ 2.29-2.42 (m, 2H), 3.39-4.16 (m, 12H, several signals overlapping), 7.08-7.15 (m, 1H), 7.29-7.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$)[a] δ 39.53, 40.32, 40.51, 44.26, 44.84, 46.05, 52.21, 52.69, 53.14, 53.29, 87.60, 88.49, 88.85, 126.46, 126.54, 129.01, 130.49, 131.04, 132.56, 139.50, 139.89, 154.49, 171.88; HRMS (ESI(+)-MS) *m/z* calcd. for $C_{15}H_{17}Cl_2NO_5Na$: 384.0381; found: 384.0283. [a]Mixture of rotamers and diastereoisomers.

Dimethyl 2-methoxy-4-(4-nitrophenyl)pyrrolidine-1,2-dicarboxylate (**14**) (Table 3, entry 6): IR (KBr) ν_{max}/cm^{-1} 3505, 3080, 2955, 2849, 1758, 1713, 1601, 1522, 1348, 1084, 738; ^{1}H NMR (300 MHz, $CDCl_3$)[a] δ 2.25-2.46 (m, 1H), 2.47-2.78 (m, 1H), 3.25-3.83 (m, 12H, several signals overlapping), 7.43 (d, 2H, *J* 8.75 Hz), 8.21 (d, 2H, *J* 8.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$)[a] δ 40.92, 45.60, 52.41, 52.88, 52.99, 53.07, 53.82, 92.71, 123.93, 128.09, 147.11, 155.23, 169.55; HRMS (ESI(+)-MS) *m/z* calcd. for $C_{13}H_{15}N_2O_5$ (M–CO_2Me): 279.0981; found: 279.0956. [a]Mixture of rotamers and diastereoisomers.

Dimethyl 2-methoxy-4-(3-nitrophenyl)pyrrolidine-1,2-dicarboxylate (**15**) (Table 3, entry 7): IR (KBr) ν_{max}/cm^{-1} 3021, 2955, 1758, 1707, 1531, 1446, 1348, 1348, 1316, 1258, 1202, 1125, 1086, 1051, 1019, 977; ^{1}H NMR (300 MHz, $CDCl_3$)[a] δ 2.28-2.61 (m, 2H), 3.42-4.19 (m, 12H, several signals overlapping), 7.44 (m, 2H), 8.19 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$)[a] δ 40.75, 41.30, 45.62, 46.00, 52.46, 52.92, 53.03, 53.11, 53.95, 92.69, 122.07, 122.37, 122.56, 129.73, 129.79, 133.52, 133.81, 141.66, 148.48, 169.98, 178.01; HRMS (ESI(+)-MS) *m/z* calcd. for $C_{14}H_{15}N_2O_6$ (M–OMe): 307.0930; found: 307.0933. [a]Mixture of rotamers and diastereoisomers.

Dimethyl 2-methoxy-4-(4-((methoxycarbonyl)amino) phenyl)pyrrolidine-1,2-dicarbo-xylate (**16**) (Table 3, entry 8): IR (KBr) ν_{max}/cm^{-1} 3328, 3055, 2995, 2954, 1755, 1712, 1615, 1600, 1536, 1370, 1229; ^{1}H NMR (300 MHz, $CDCl_3$)[a] δ 2.35-2.40 (m, 2H), 3.46-4.03 (m, 15H, several signals overlapping), 6.63 (sl, 1H), 7.20 (d, 2H, *J* 7.5 Hz), 7.34 (d, 2H, *J* 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$)[a] δ 39.81, 45.56, 45.84, 46.15, 52.14, 52.35, 52.79, 52.87, 52.99, 54.43, 92.92, 119.01, 127.79, 134.45, 136.87, 153.98, 155.46, 170.01; HRMS (ESI(+)-MS) *m/z* calcd. for $C_{15}H_{19}N_2O_5$ (M–CO_2Me = 307.1294); found 307.1289. [a]Mixture of rotamers and diastereoisomers.

Reference

1. Armarego, W. L. F.; Perrin, D. D.; *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, 1998.

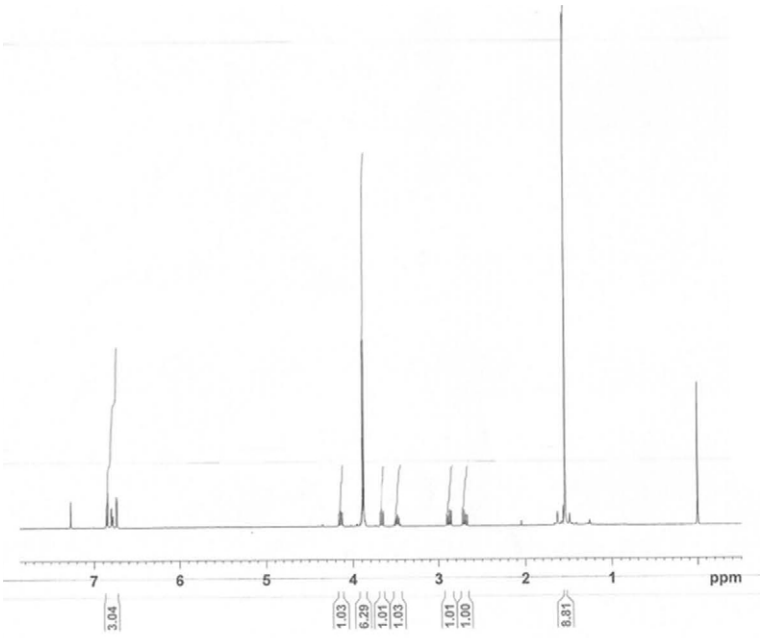

Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **3**.

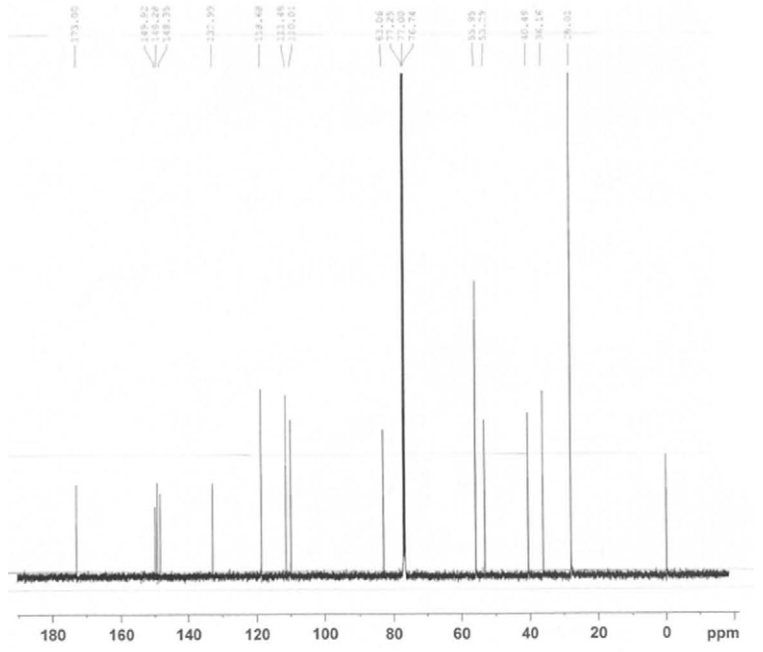

Figure S2. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **3**.

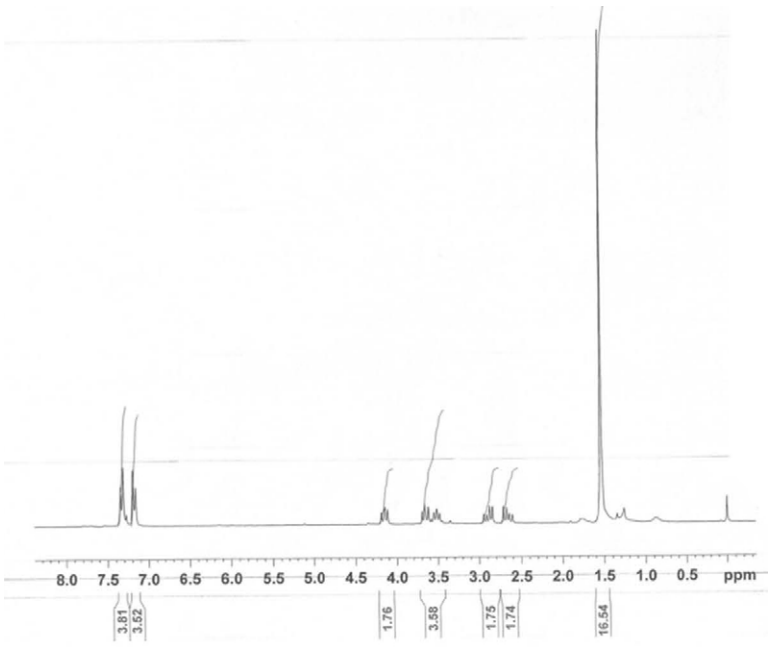

Figure S3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **4**.

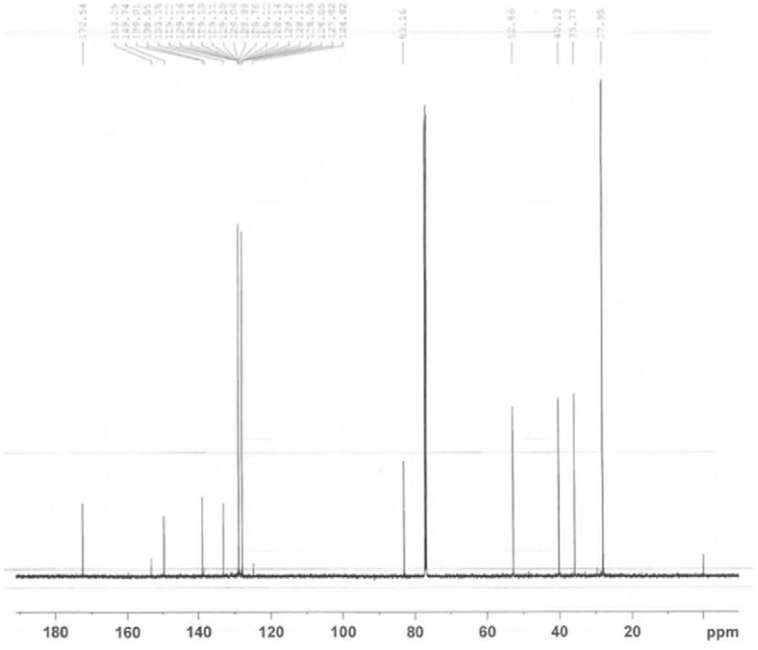

Figure S4. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **4**.

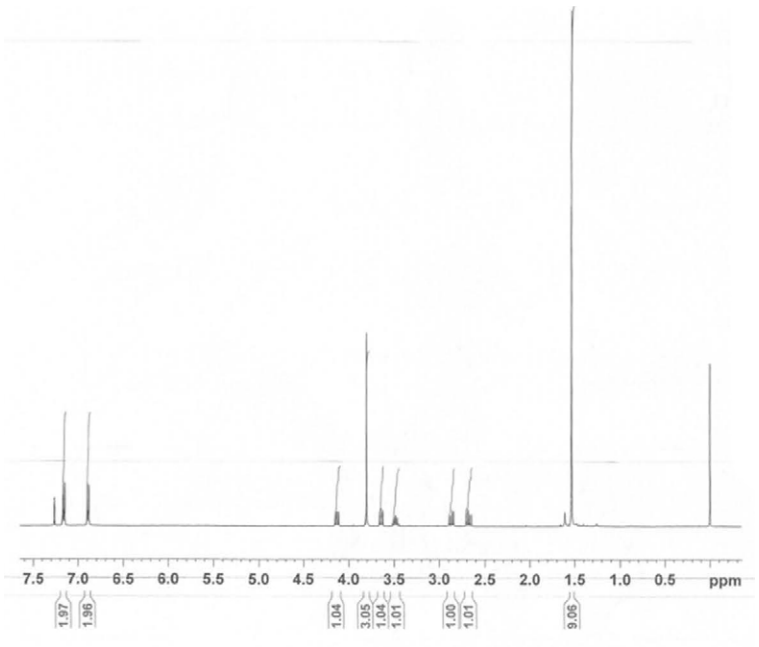

Figure S5. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **5**.

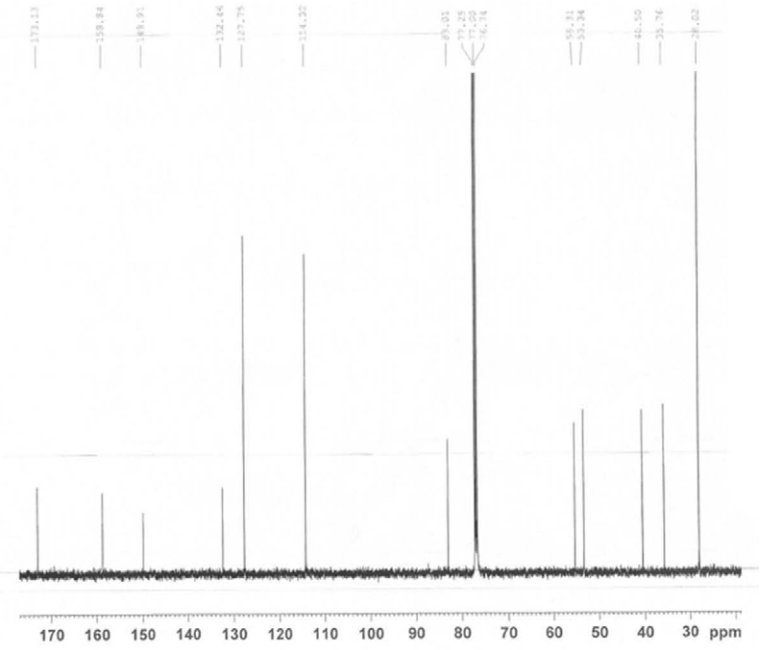

Figure S6. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **5**.

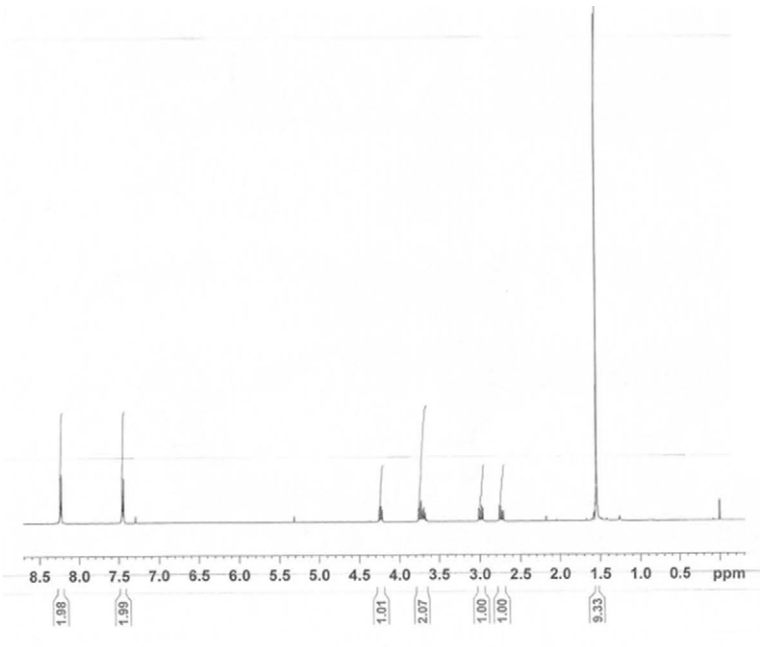

Figure S7. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **6**.

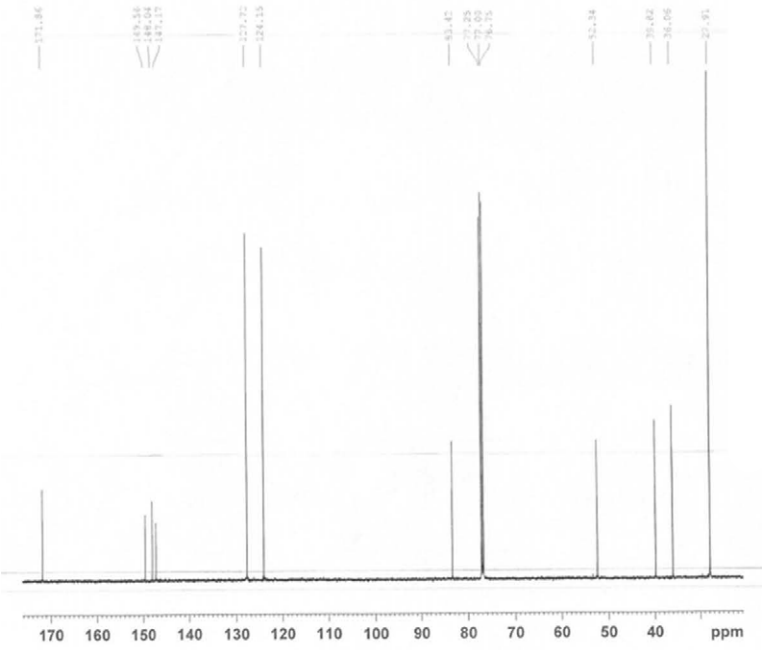

Figure S8. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **6**.

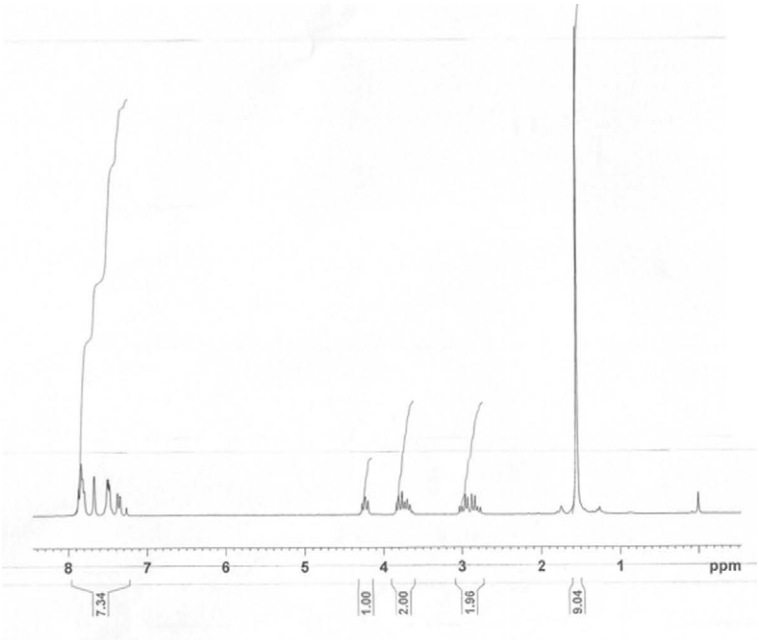

Figure S9. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **7**.

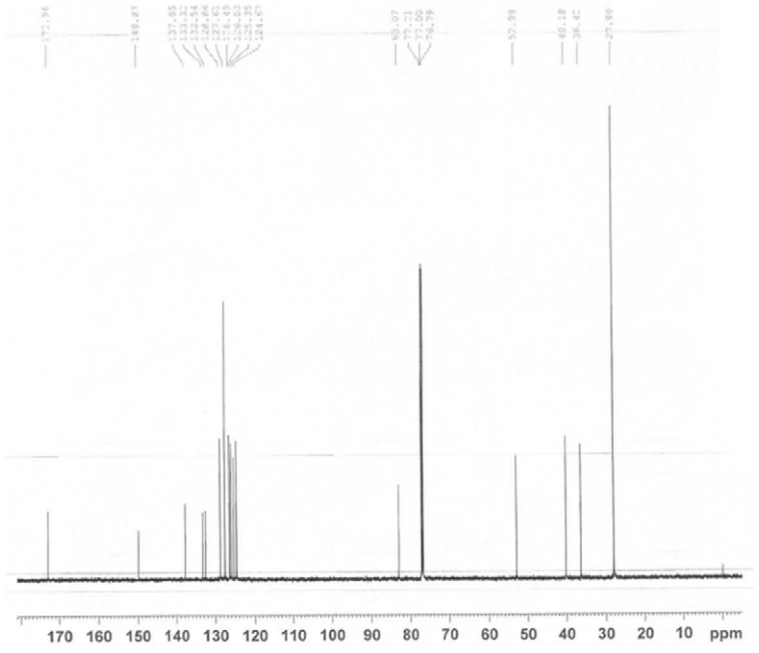

Figure S10. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **7**.

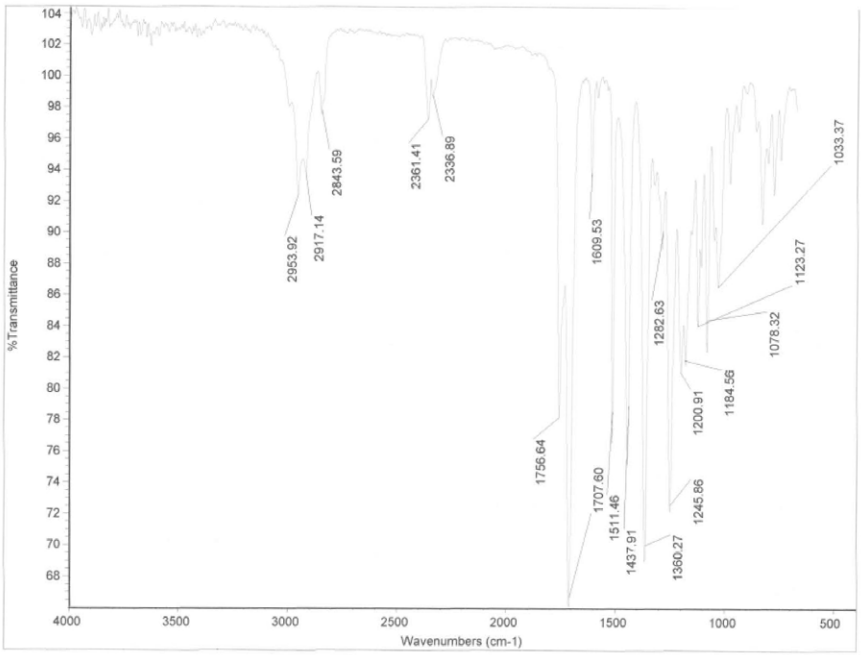

Figure S11. IR spectrum (film) of compound **8**.

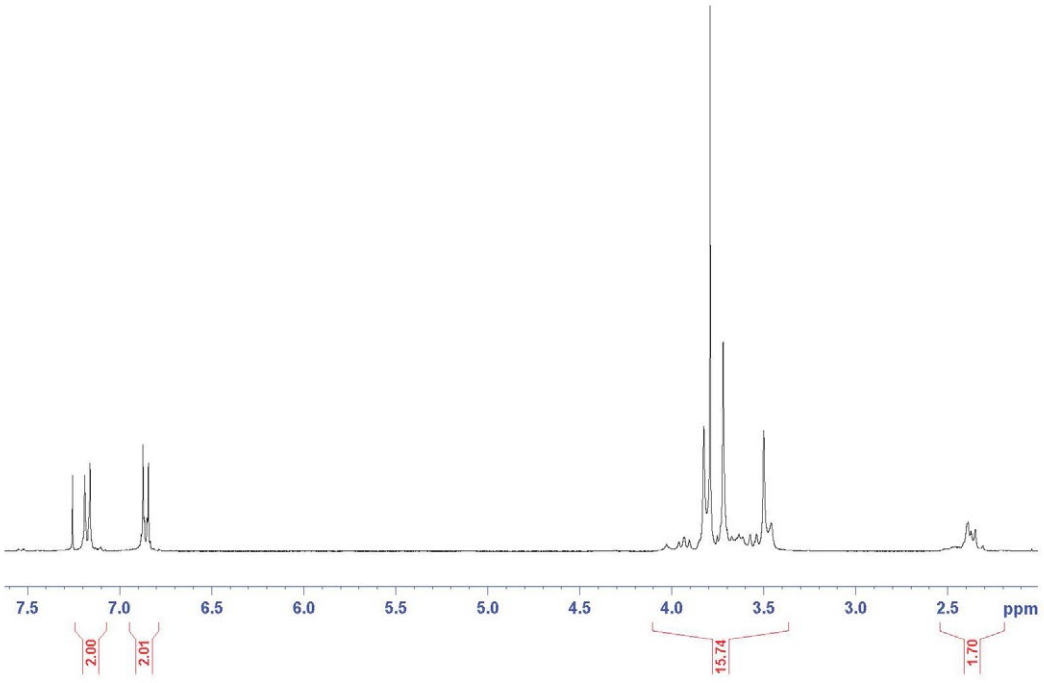

Figure S12. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **8**.

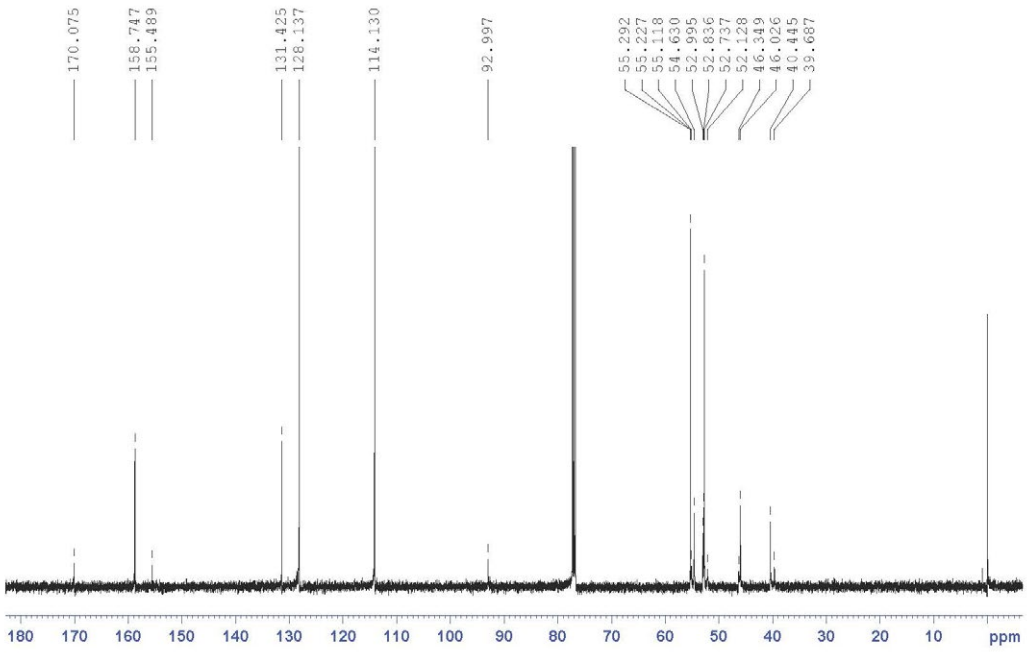

Figure S13. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **8**.

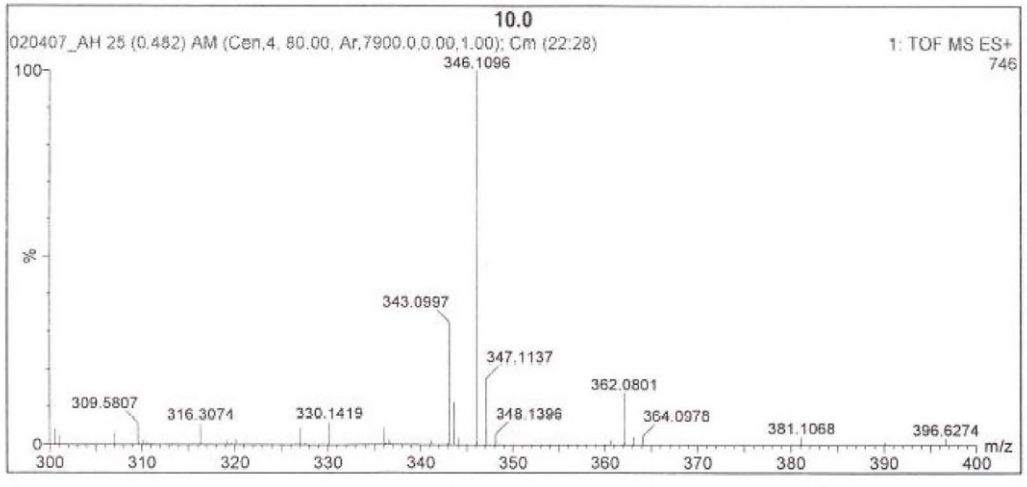

Figure S14. HRMS ESI(+)-MS spectrum of compound **8**.

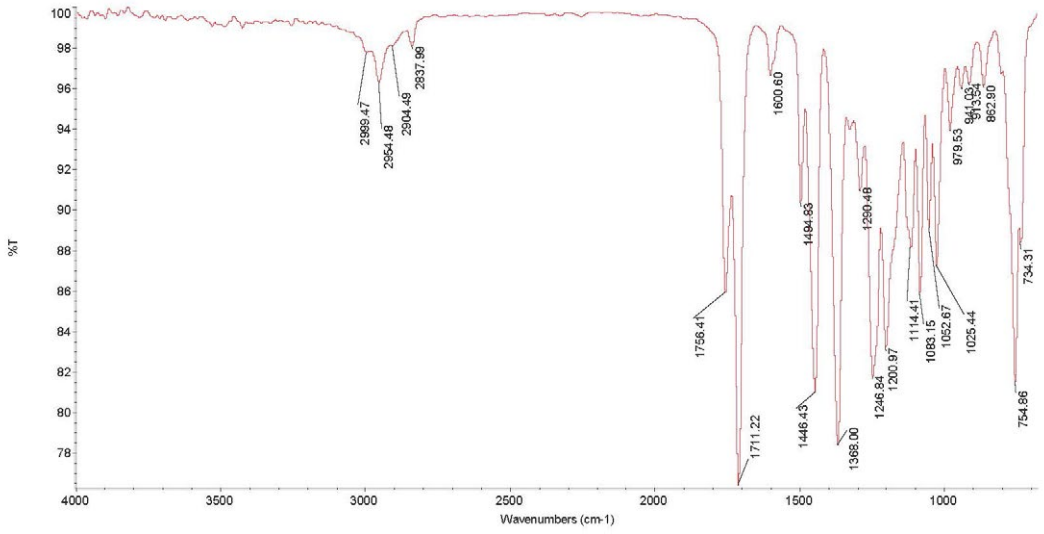

Figure S15. IR spectrum (film) of compound **9**.

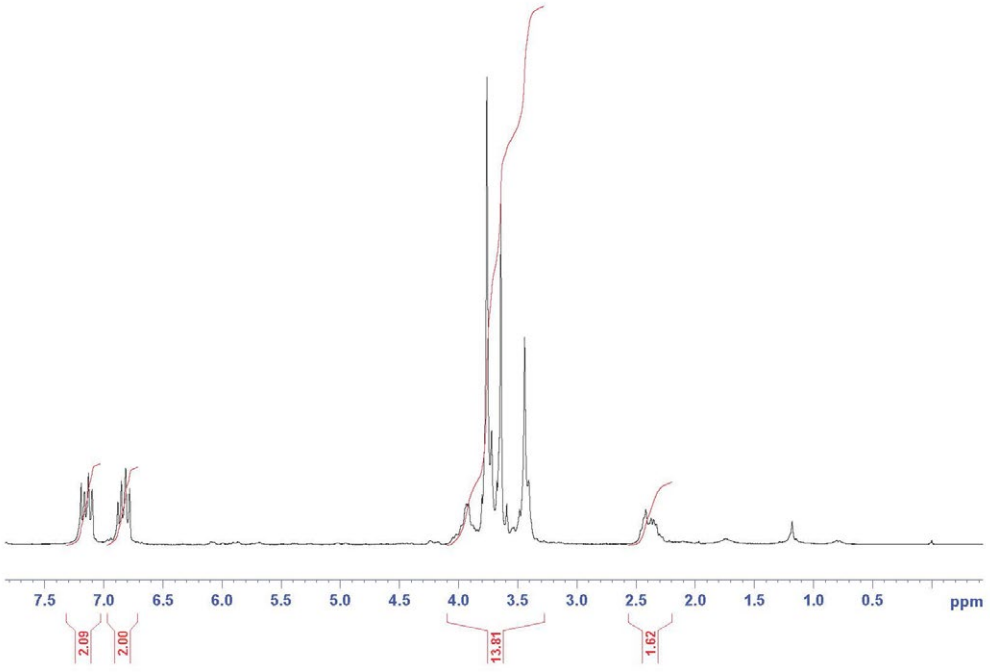

Figure S16. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **9**.

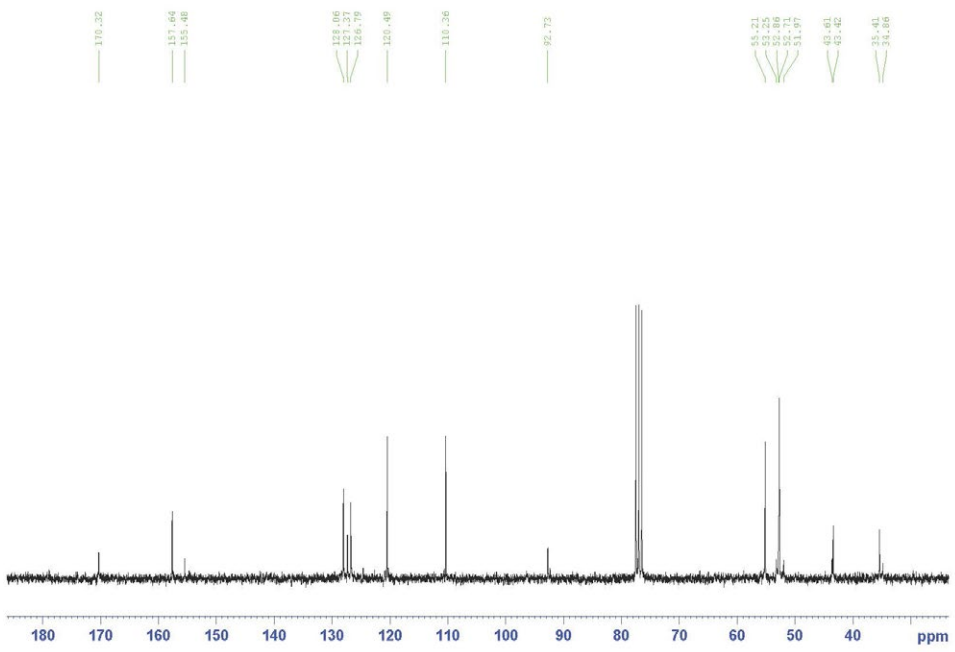

Figure S17. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **9**.

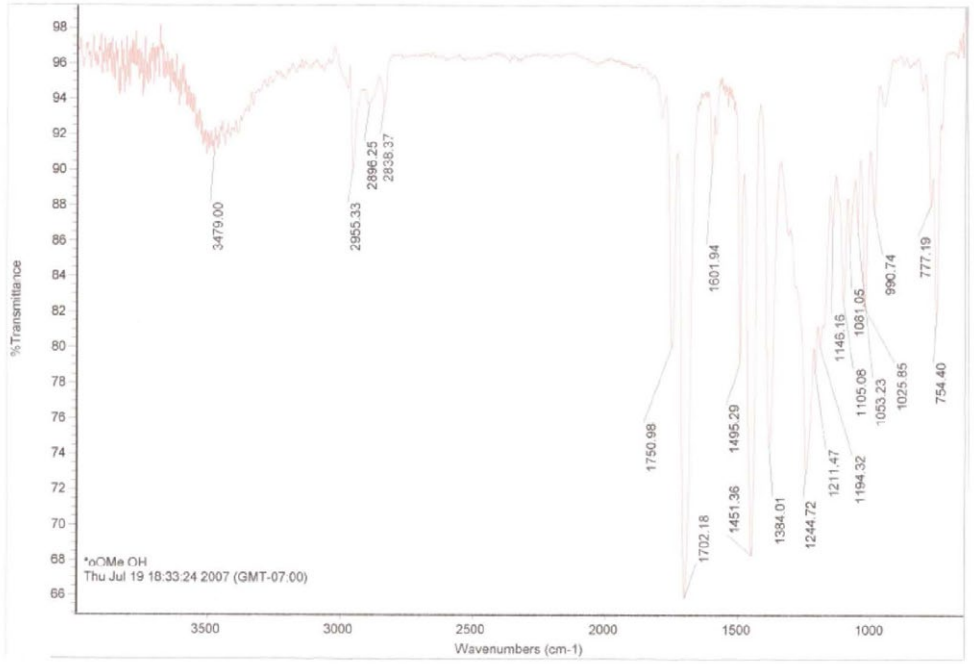

Figure S18. IR spectrum (film) of compound **10**.

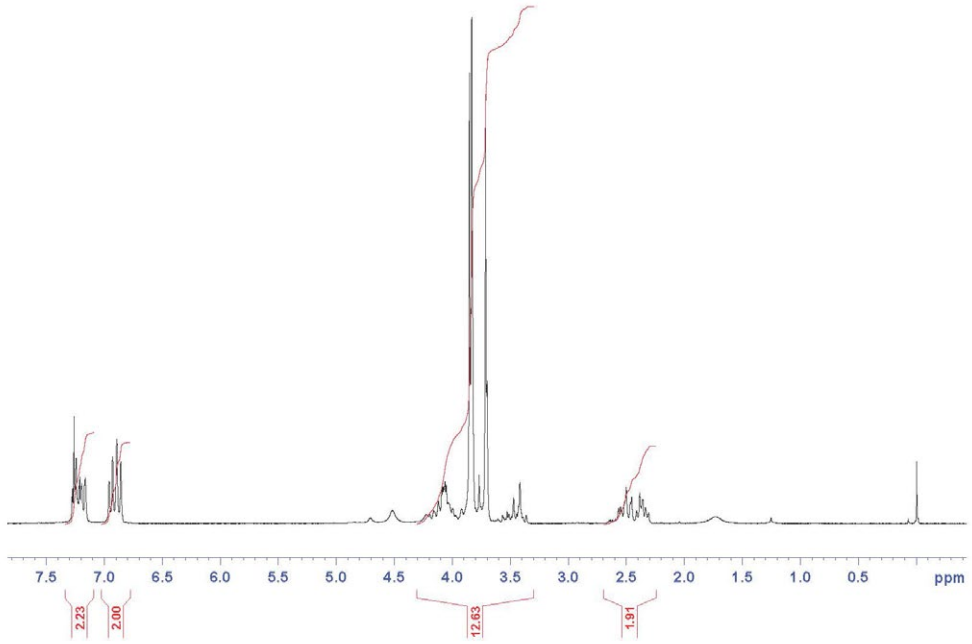

Figure S19. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **10**.

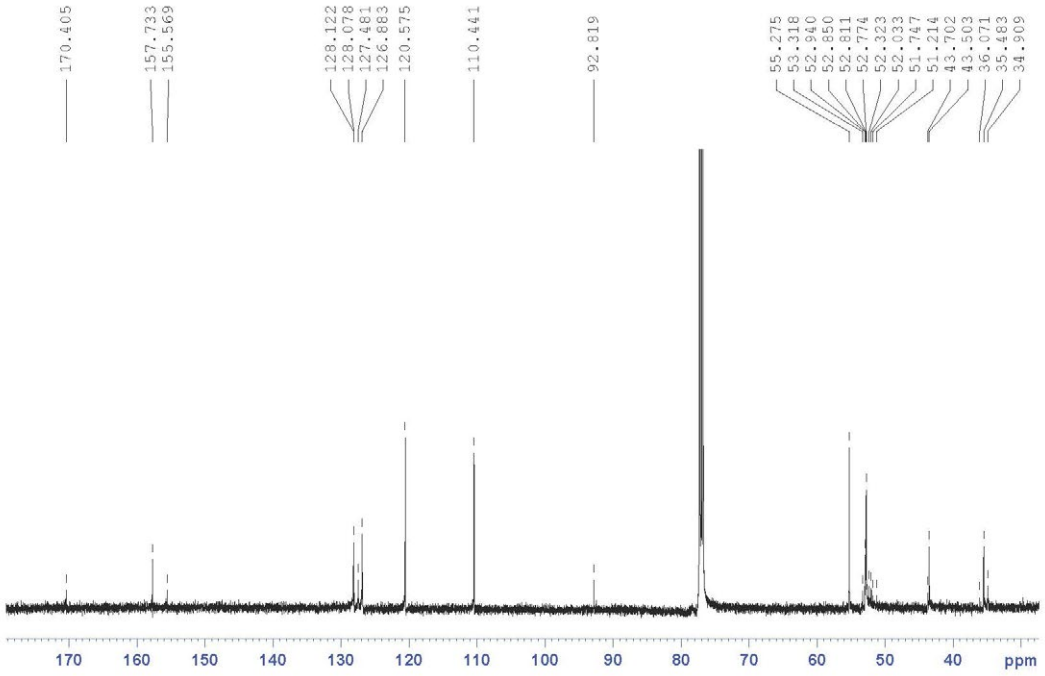

Figure S20. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **10**.

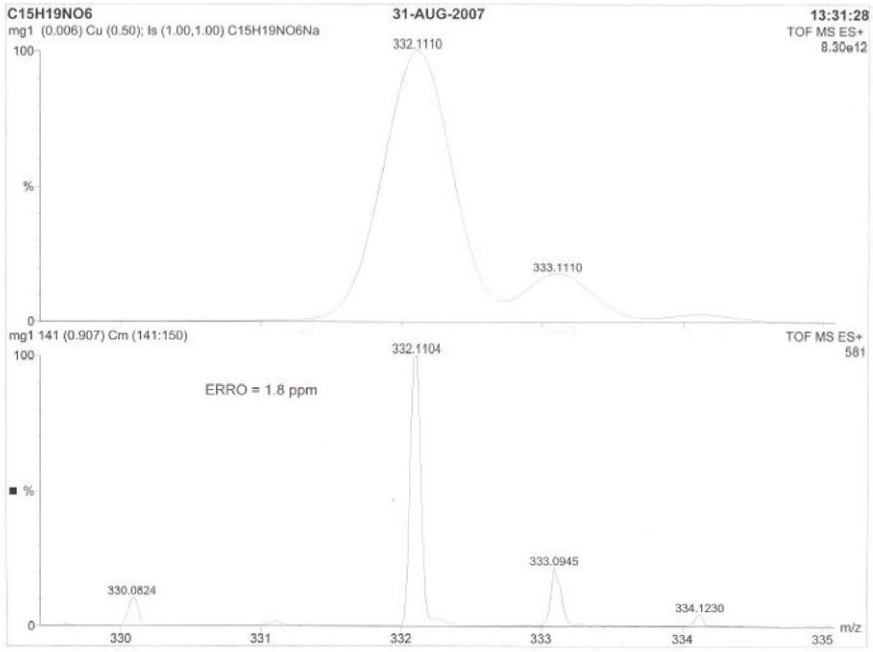

Figure S21. HRMS ESI(+)-MS spectrum of compound **10**.

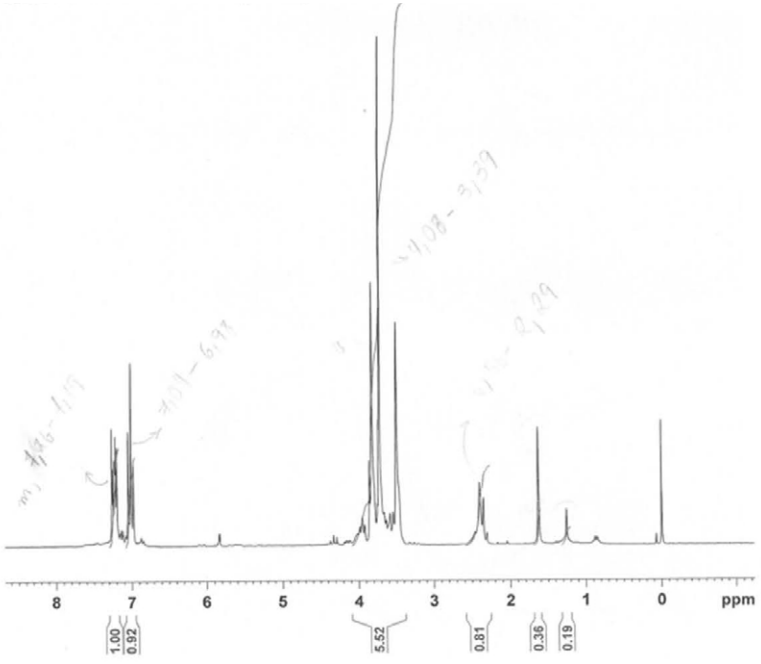

Figure S22. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **11**.

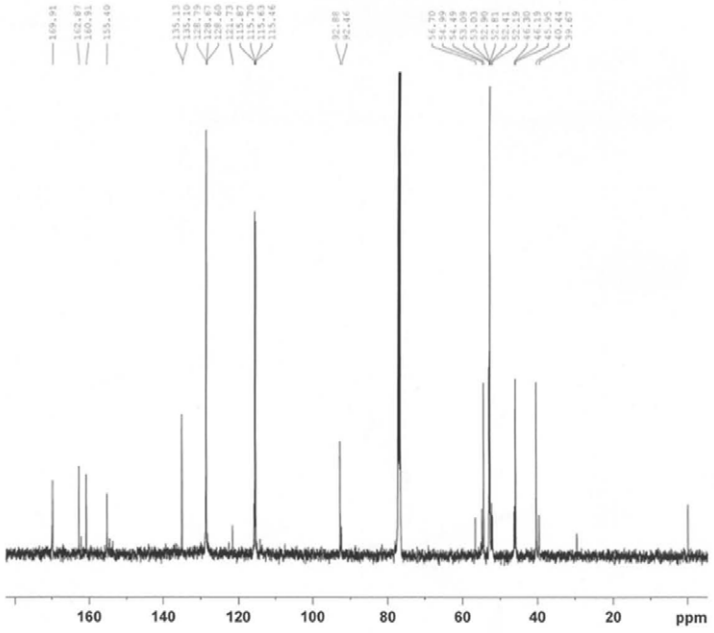

Figure S23. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **11**.

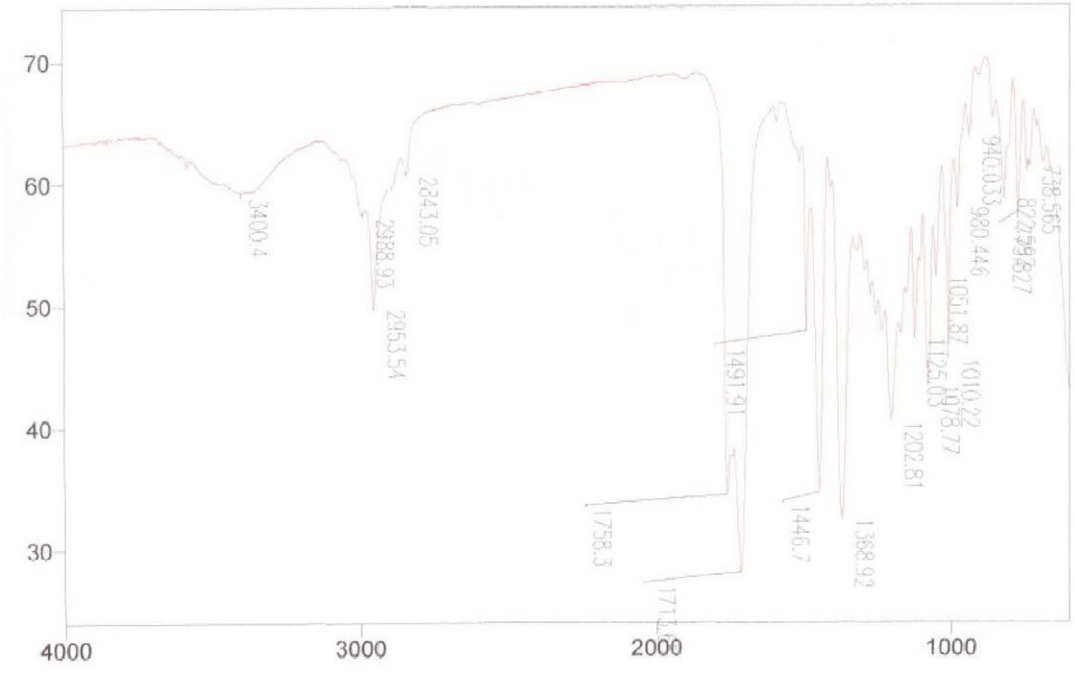

Figure S24. IR spectrum (film) of compound **12**.

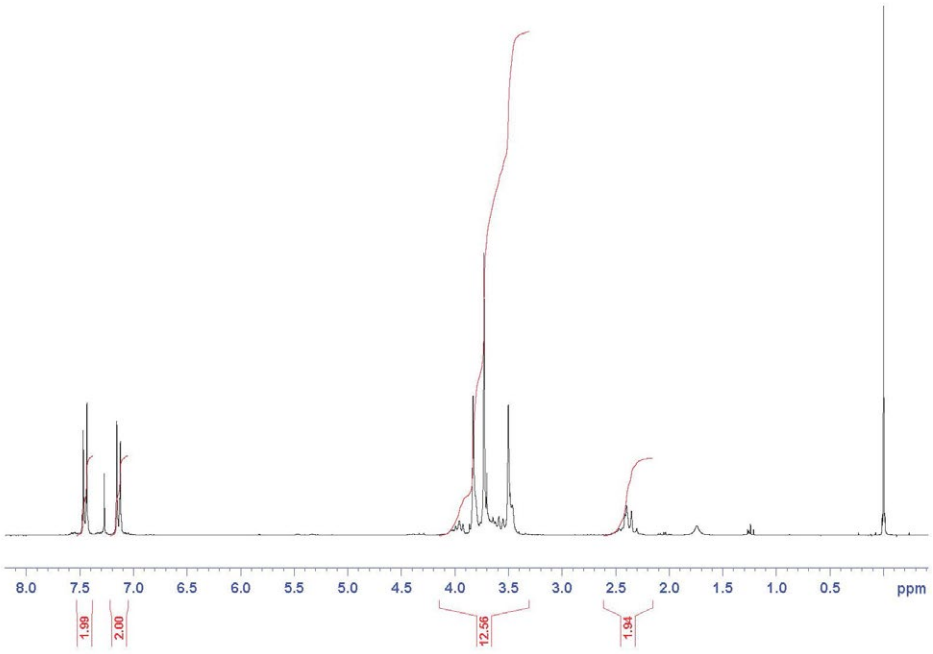

Figure S25. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **12**.

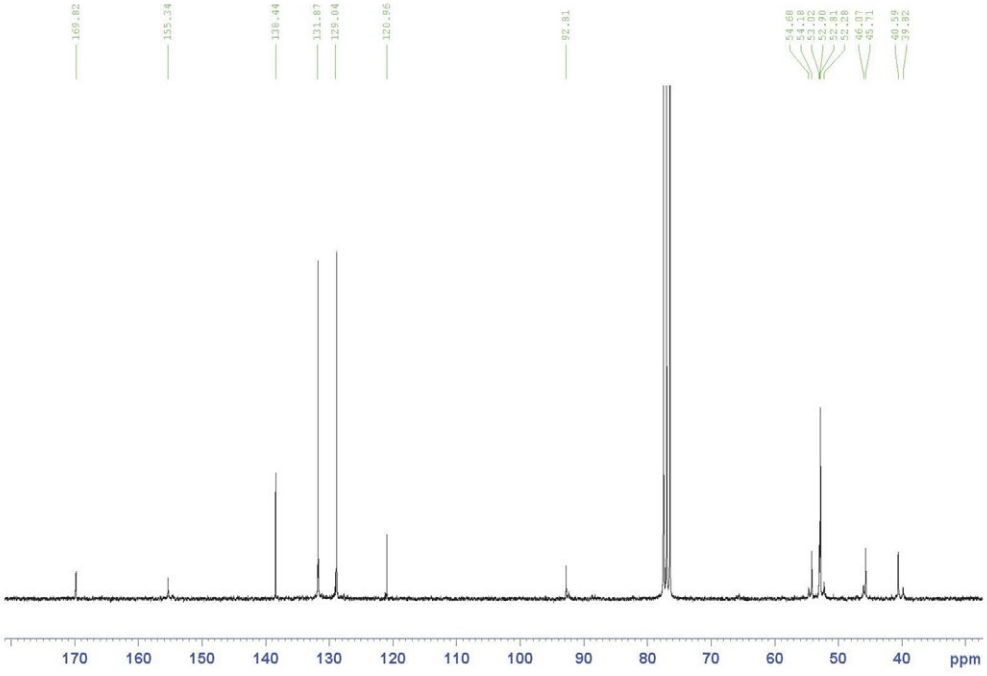

Figure S26. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **12**.

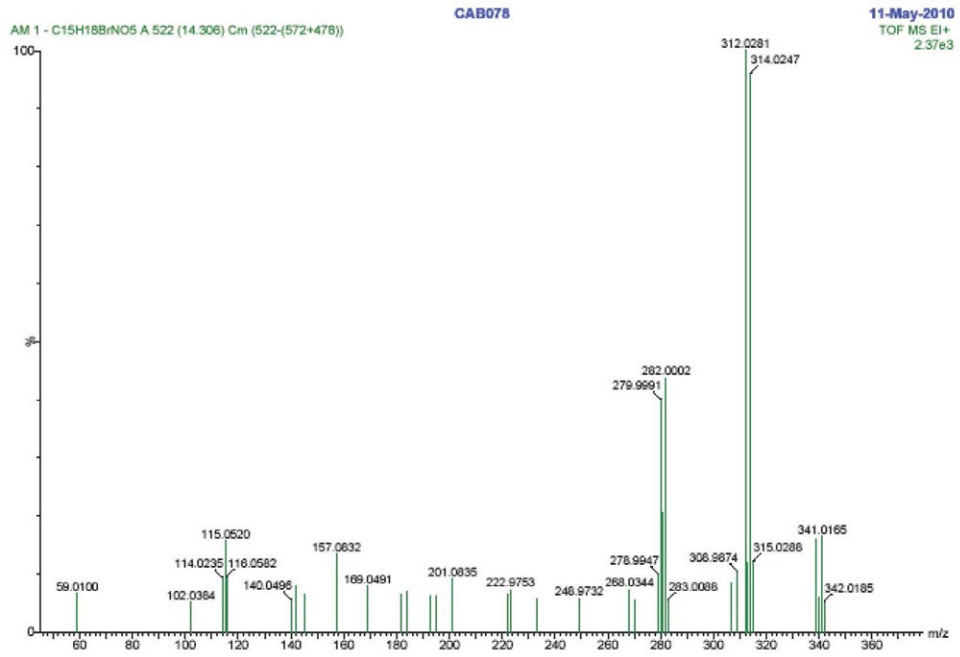

Figure S27. HRMS (EI) spectrum of compound **12**.

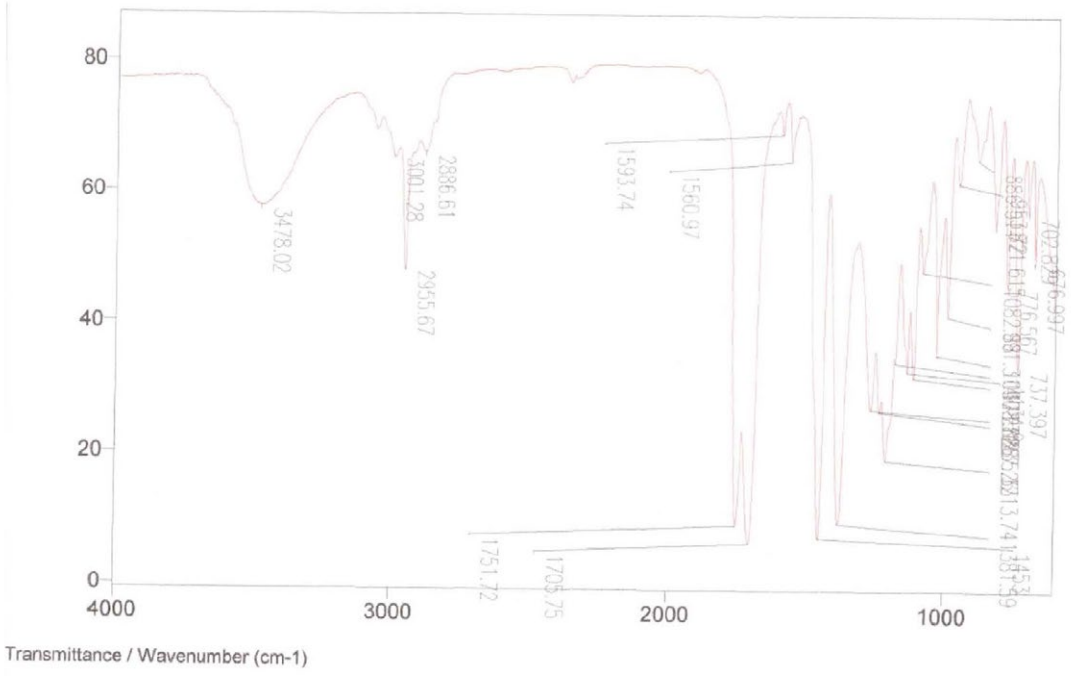

Figure S28. IR spectrum (film) of compound **13**.

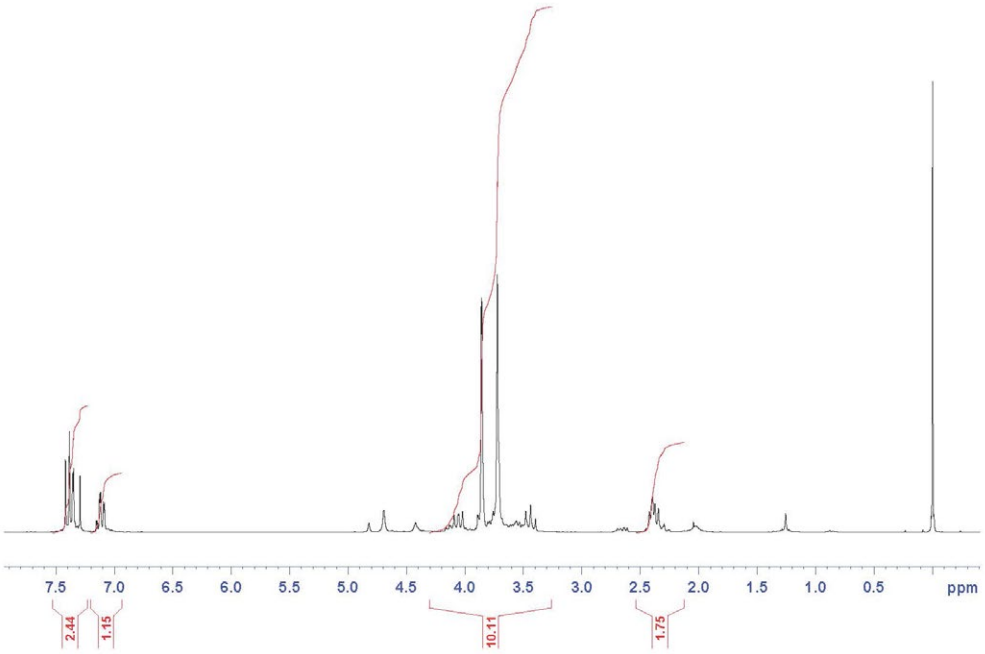

Figure S29. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **13**.

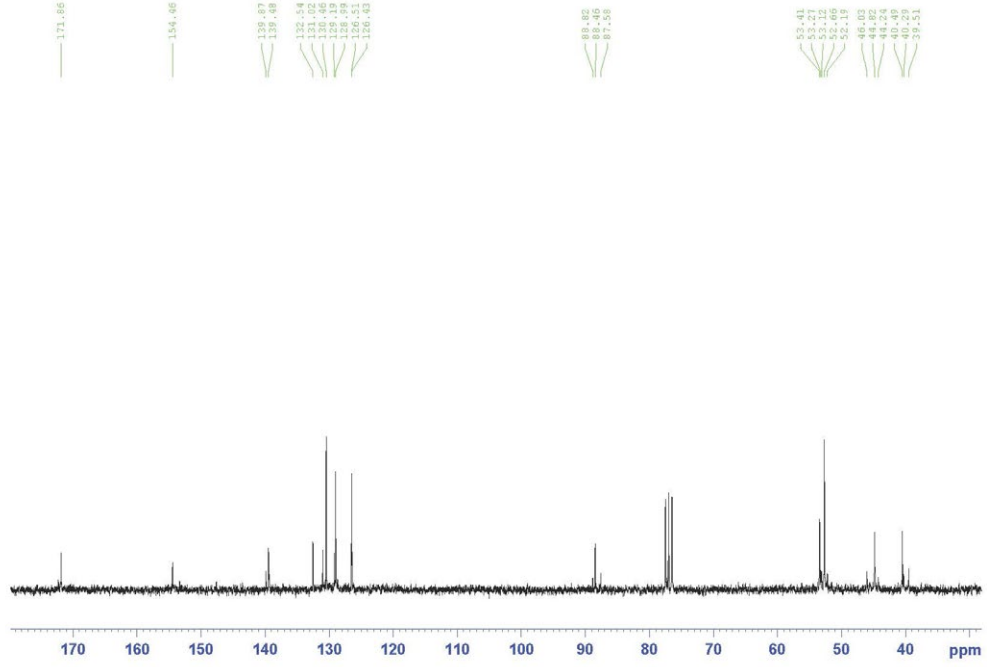

Figure S30. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **13**.

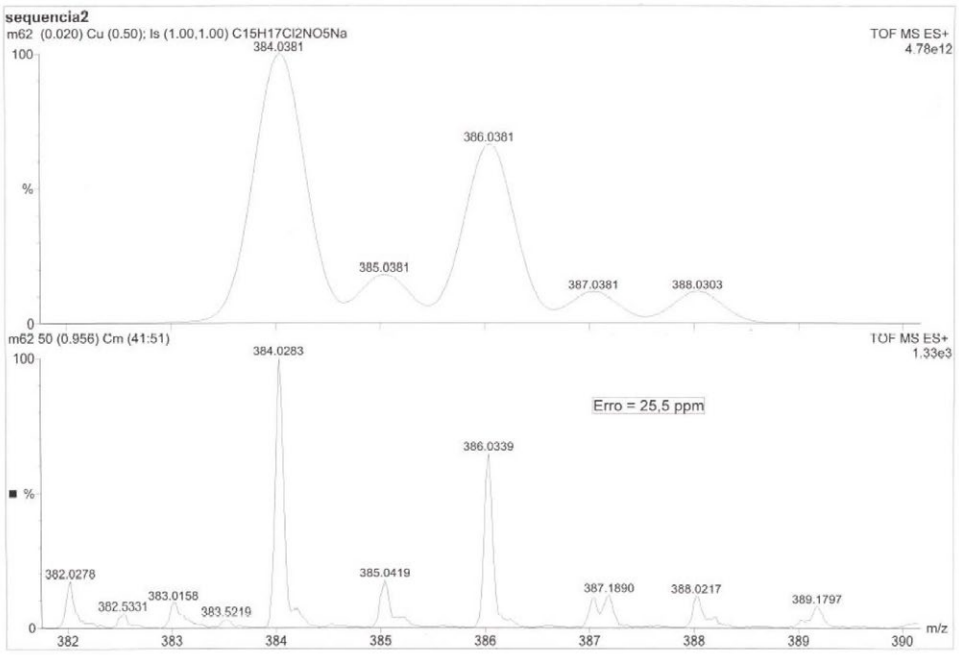

Figure S31. HRMS ESI(+)-MS spectrum of compound **13**.

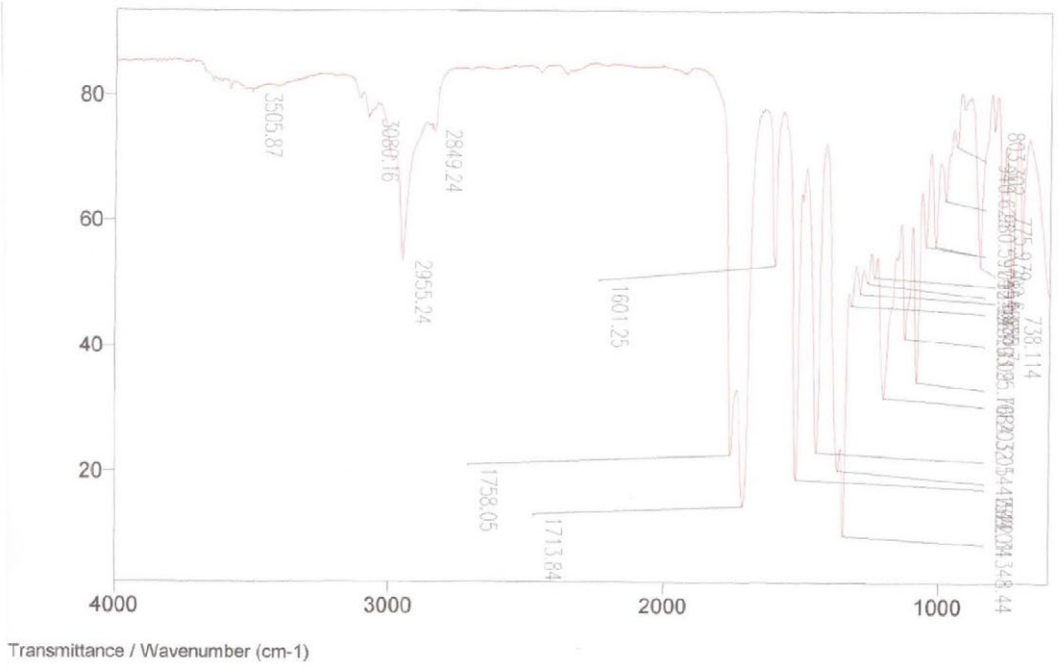

Figure S32. IR spectrum (film) of compound **14**.

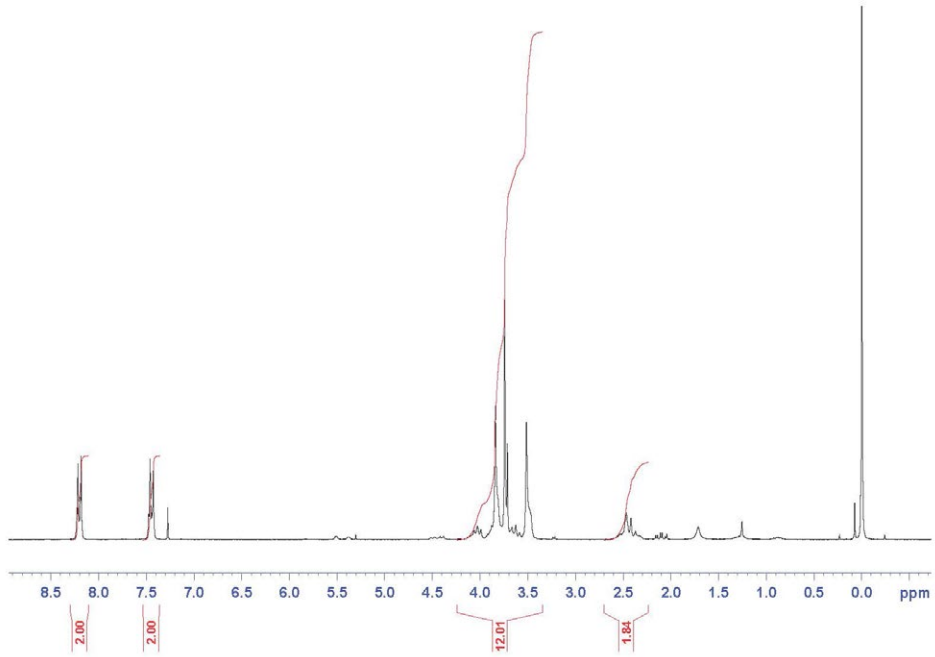

Figure S33. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **14**.

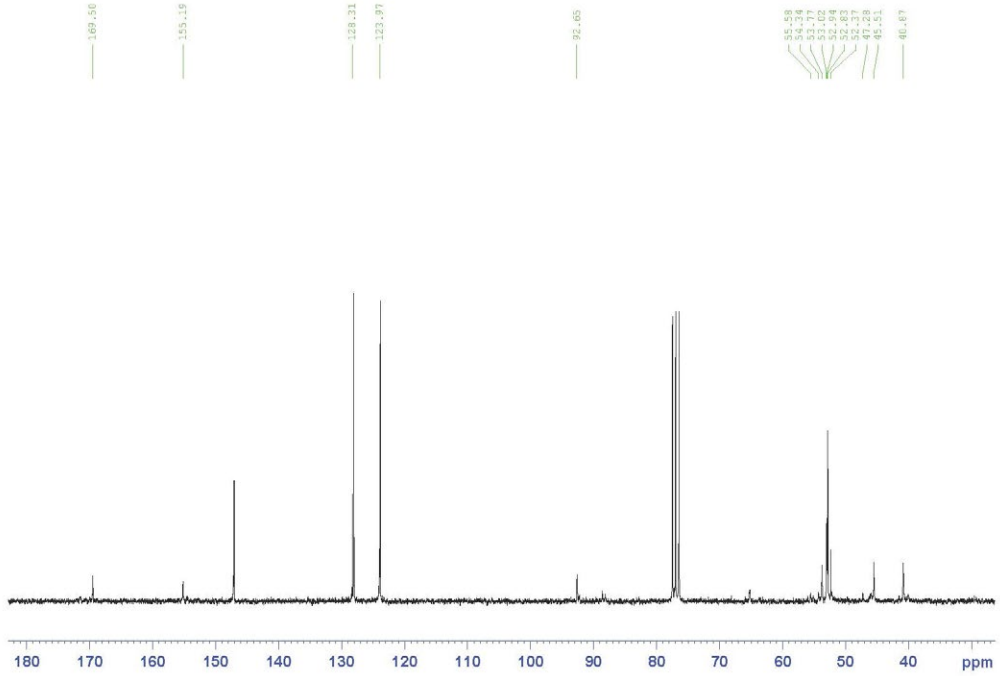

Figure S34. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **14**.

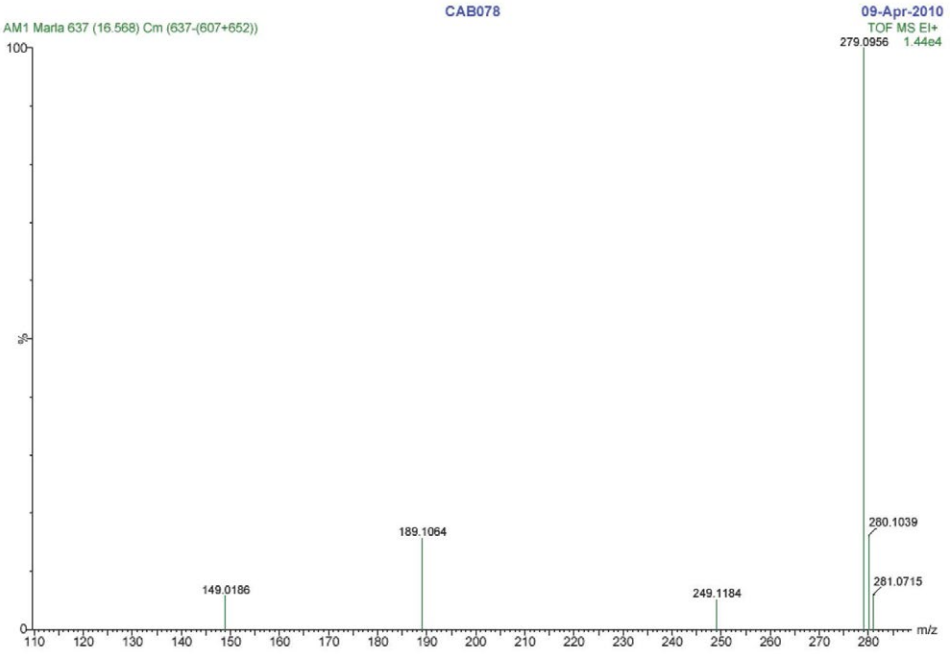

Figure S35. HRMS (EI) spectrum of compound **14**.

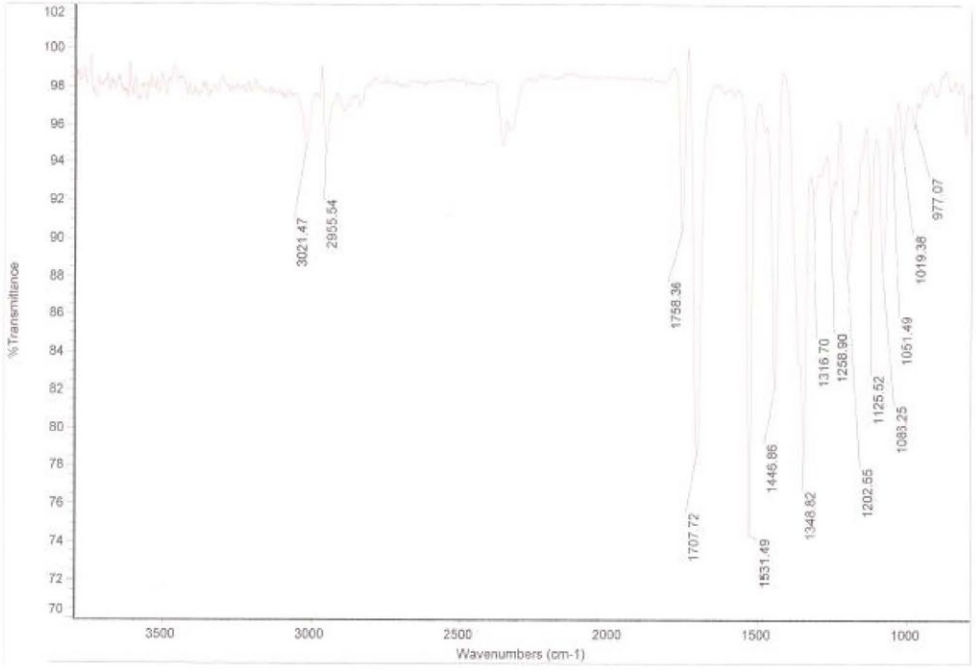

Figure S36. IR spectrum (film) of compound **15**.

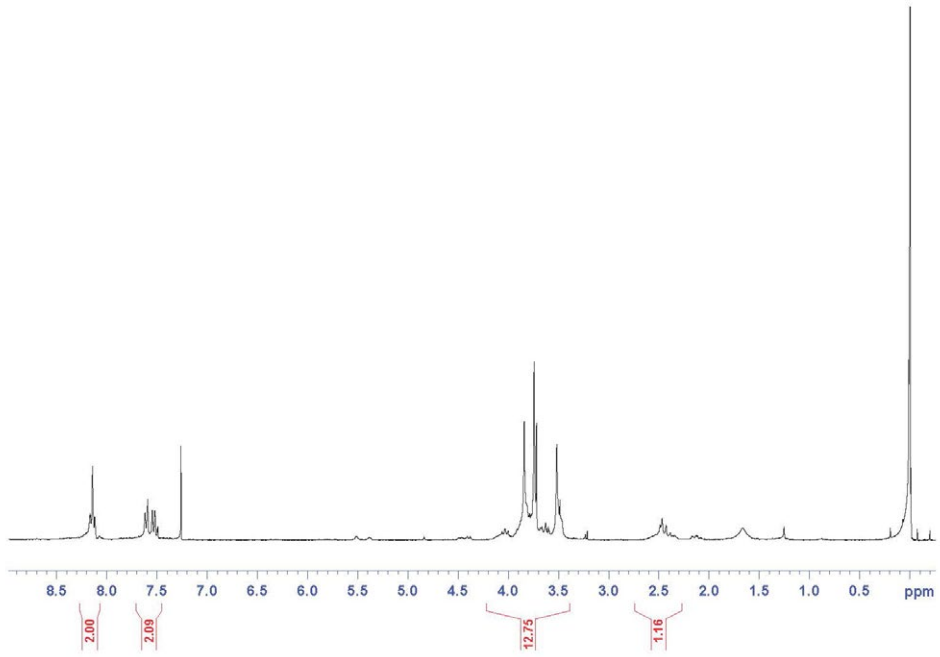

Figure S37. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **15**.

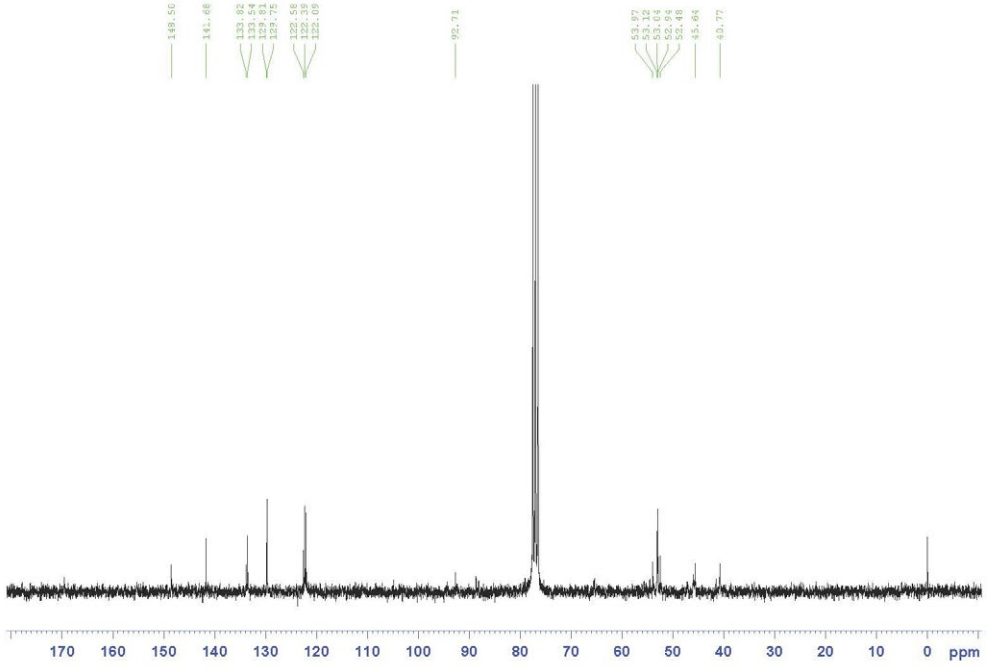

Figure S38. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **15**.

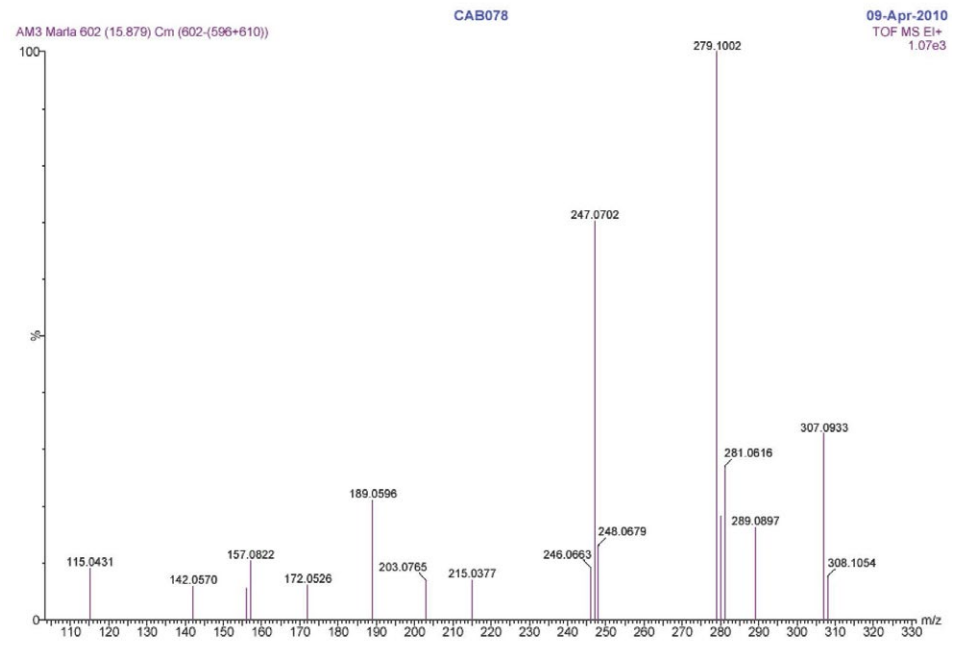

Figure S39. HRMS (EI) spectrum of compound **15**.

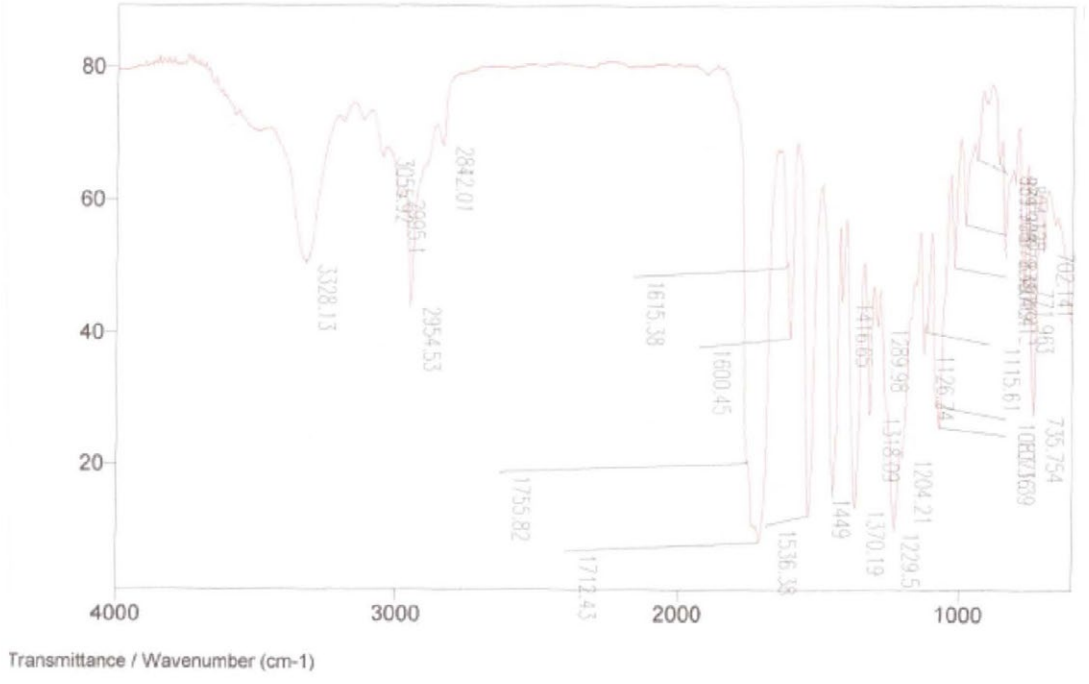

Figure S40. IR spectrum (film) of compound **16**.

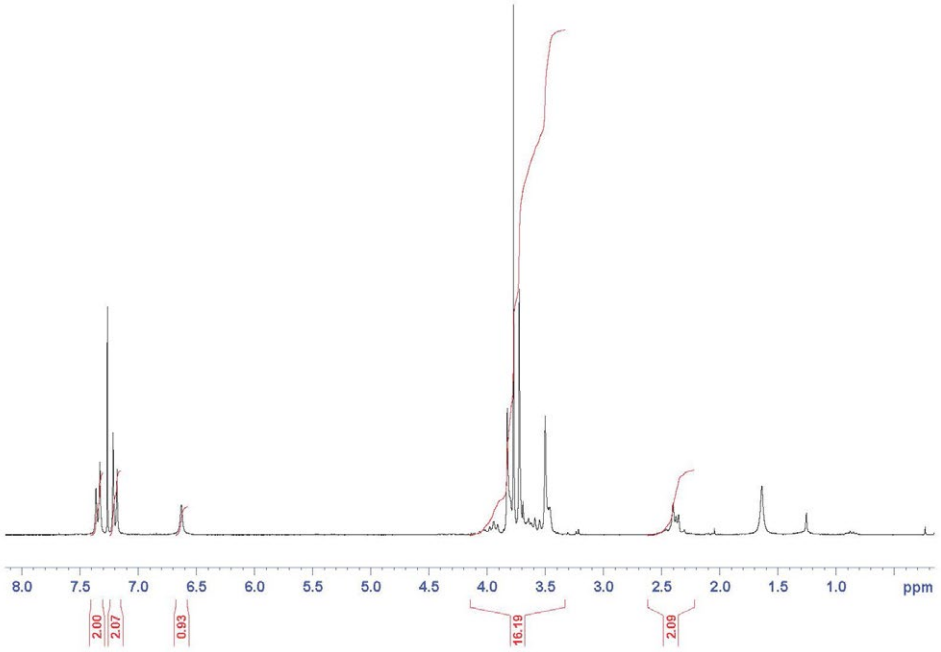

Figure S41. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **16**.

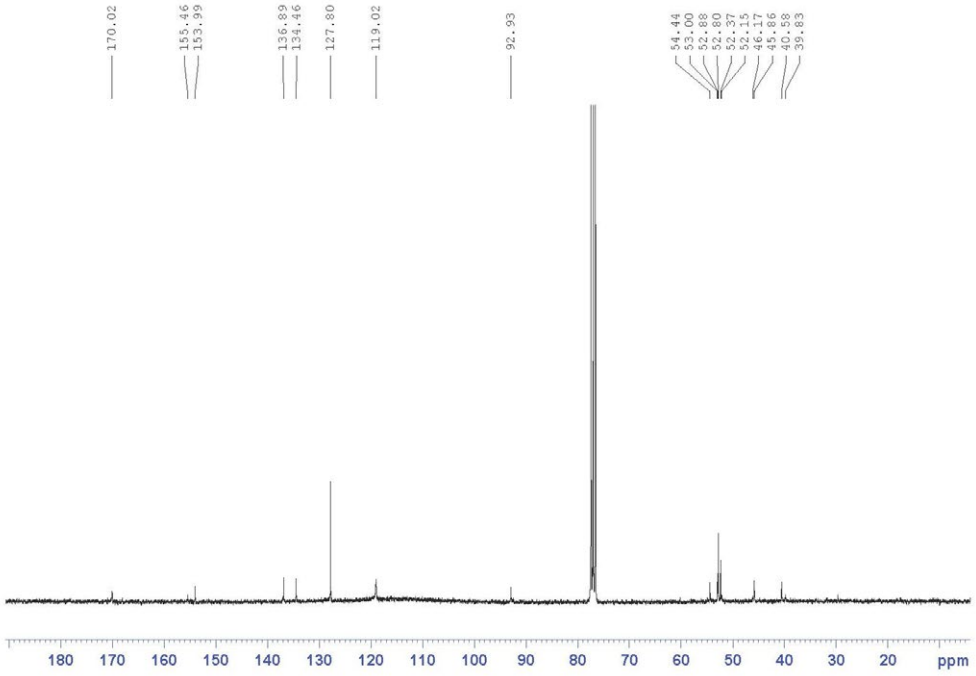

Figure S42. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **16**.

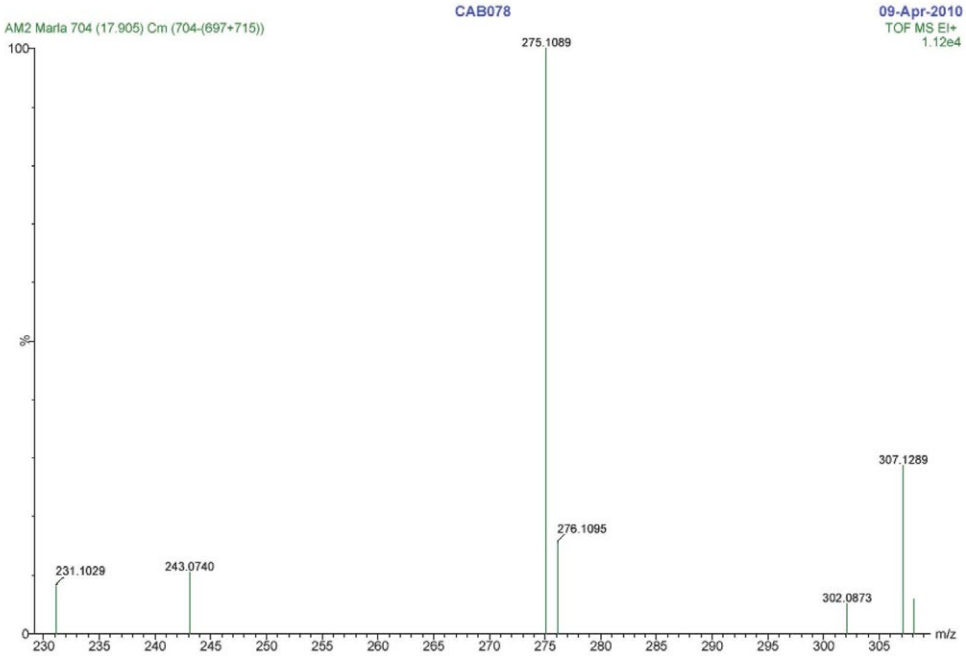

Figure S43. HRMS (EI) spectrum of compound **16**.