**Table S1.** Refinement parameters and crystal data for **L1** and **L2.**

| CCDC Deposition Number | L1: 1522882 | L2: 1523265 |
|---|---|---|
| Molecular Formula | $C_{18}H_{16}N_4O_3$ | $C_{18}H_{16}N_4O$ |
| Molecular Weight | 336.12 | 304.13 |
| Crystal System | Monoclinic | Monoclinic |
| Space Group | $P2_1/c$ | C2/c |
| a (Å) | 8.1405 (4) | 18.2409 (13) |
| b (Å) | 24.3478 (13) | 14.7347 (13) |
| c (Å) | 12.0975 (6) | 13.1676 (9) |
| β (°) | 114.087 (3) | 106.072 (3) |
| V (Å$^3$) | 2188.98 (19) | 3400.8 (5) |
| Z | 4 | 8 |
| Dcalc (g·cm$^{-3}$) | 1.297 | 1.189 |
| Crystal Dimension (mm) | 0.36 × 0.28 × 0.14 | 0.42 × 0.22 × 0.07 |
| μ (mm$^{-1}$) | 0.10 | 0.08 |
| Tmin/Tmax | 0.635/ 0.884 | 0.969/ 0.995 |
| Measured Reflections | 32643 | 61162 |
| Indices Range (h, k, l) | −10/10, −31/31, −14/15 | −23/23, −19/19, −17/17 |
| θ Limit (°) | 27.5-2.5 | 27.5-2.2 |
| Unique Reflections | 5028 | 3907 |
| Observed Reflections (I > 2σ(I)) | 2561 | 2181 |
| Parameters | 308 | 217 |
| Goodness of Fit on $F^2$ | 1.01 | 1.03 |
| $R_1$,$wR_2$ [I > 2σ(I)] | 0.0585/ 0.1548 | 0.0561/ 0.1514 |

**Table S2.** Selected geometric parameters (Å, °) for **L1**

| | | | |
|---|---|---|---|
| O1—C10 | 1.227 (3) | N2—C9 | 1.346 (3) |
| O2—C14 | 1.363 (3) | N3—N4 | 1.383 (3) |
| O2—C18 | 1.417 (4) | N3—C10 | 1.341 (3) |
| O3—C15 | 1.363 (3) | N4—C11 | 1.274 (3) |
| O4—C21 | 1.200 (6) | N5—C21 | 1.313 (5) |
| N1—N2 | 1.339 (3) | N5—C19 | 1.444 (5) |
| N1—C7 | 1.334 (3) | N5—C20 | 1.445 (4) |
| C14—O2—C18 | 118.3 (2) | N2—C9—C8 | 106.0 (2) |
| N2—N1—C7 | 105.30 (19) | O1—C10—N3 | 122.8 (2) |
| N1—N2—C9 | 112.6 (2) | N3—C10—C9 | 116.0 (2) |
| N4—N3—C10 | 119.5 (2) | O1—C10—C9 | 121.3 (2) |
| N3—N4—C11 | 114.9 (2) | N4—C11—C12 | 122.9 (2) |
| C19—N5—C20 | 116.9 (3) | O2—C14—C13 | 125.7 (2) |

| | | | |
|---|---|---|---|
| C19—N5—C21 | 122.6 (3) | O2—C14—C15 | 114.2 (2) |
| C20—N5—C21 | 120.6 (3) | O3—C15—C14 | 117.2 (2) |
| N1—C7—C6 | 120.8 (2) | O3—C15—C16 | 123.4 (2) |
| N1—C7—C8 | 110.0 (2) | O4—C21—N5 | 126.3 (4) |
| N2—C9—C10 | 118.7 (2) | | |

**Table S3** Hydrogen-bond geometry (Å, °) for **L1**

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H1N3···O3$^{i}$ | 0.87 (3) | 2.24 (3) | 3.067 (3) | 160 (2) |
| O3—H1O3···O5W | 0.95 (3) | 1.71 (3) | 2.652 (3) | 171 (3) |
| N2—H1N2···O1$^{ii}$ | 0.90 (3) | 1.98 (3) | 2.811 (3) | 154 (2) |
| O5W—H2OW···O1$^{iii}$ | 0.86 (4) | 2.28 (3) | 2.936 (3) | 133 (3) |
| O5W—H2OW···N4$^{iii}$ | 0.86 (4) | 2.37 (3) | 3.160 (3) | 153 (3) |
| O5W—H1OW···N1$^{iv}$ | 1.01 (4) | 1.82 (4) | 2.823 (3) | 172 (3) |
| C8—H8A···O3$^{i}$ | 0.9300 | 2.5800 | 3.392 (3) | 147.00 |
| C13—H13A···O5W$^{v}$ | 0.9300 | 2.5500 | 3.463 (3) | 168.00 |
| C17—H17A···O4 | 0.9300 | 2.4300 | 3.316 (4) | 158.00 |

Symmetry codes: (i) *x*+1, −*y*+1/2, *z*+1/2; (ii) −*x*, −*y*+1, −*z*+1; (iii) *x*, −*y*+1/2, *z*−1/2; (iv) −*x*, *y*−1/2, −*z*+1/2; (v) *x*, −*y*+1/2, *z*+1/2.

**Table S4** Selected geometric parameters (Å, °) for **L2**

| | | | |
|---|---|---|---|
| O1—C10 | 1.226 (2) | N3—N4 | 1.382 (2) |
| N1—N2 | 1.340 (2) | N3—C10 | 1.338 (3) |
| N1—C7 | 1.349 (3) | N4—C11 | 1.266 (3) |
| N2—C9 | 1.335 (2) | | |
| N2—N1—C7 | 113.43 (15) | N2—C9—C8 | 111.44 (16) |
| N1—N2—C9 | 103.94 (15) | N2—C9—C10 | 119.43 (17) |
| N4—N3—C10 | 119.23 (17) | N3—C10—C9 | 114.96 (16) |
| N3—N4—C11 | 115.62 (18) | O1—C10—N3 | 124.01 (19) |
| N1—C7—C6 | 122.70 (17) | O1—C10—C9 | 120.99 (19) |

| | | | |
|---|---|---|---|
| N1—C7—C8 | 105.38 (18) | N4—C11—C12 | 121.9 (2) |

**Table S5** Hydrogen-bond geometry (Å, °) For **L2**

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1N1···O1$^{i}$ | 0.86 (2) | 2.00 (2) | 2.779 (2) | 151 (2) |
| N3—H1N3···N2$^{ii}$ | 0.91 (2) | 2.11 (2) | 2.976 (2) | 159.4 (19) |
| Symmetry codes: (i) *x*, −*y*+1, *z*+1/2; (ii) −*x*+1, *y*, −*z*+3/2. | | | | |

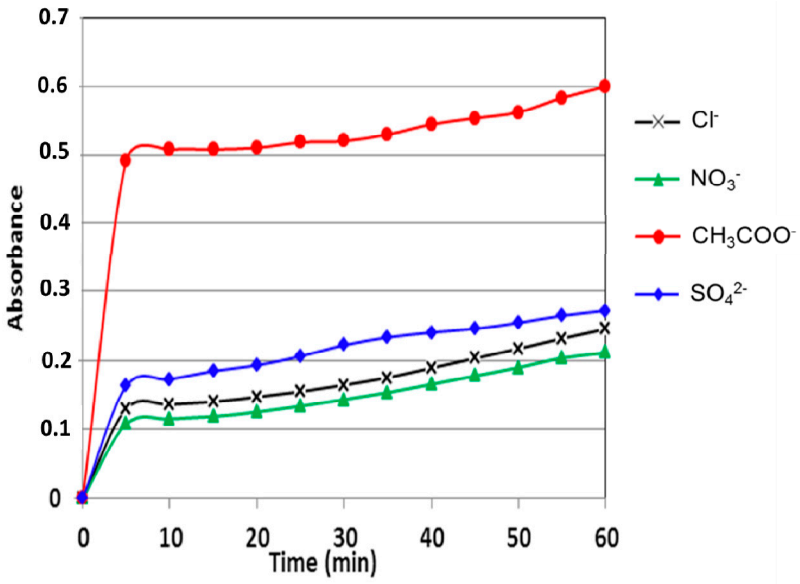


**Figure S1.** Catechol oxidation in the presence of copper complexes formed with **L1.**

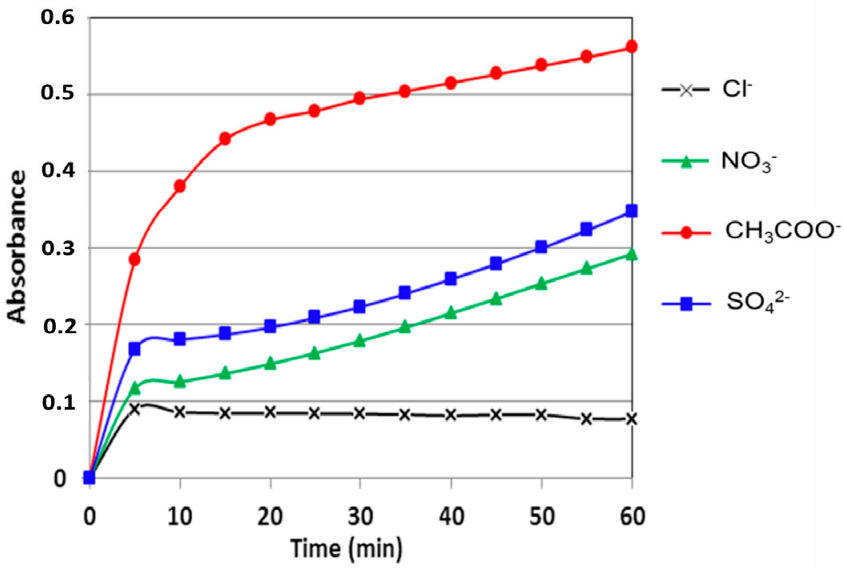


**Figure S2.** Catechol oxidation in the presence of copper complexes formed with **L2.**

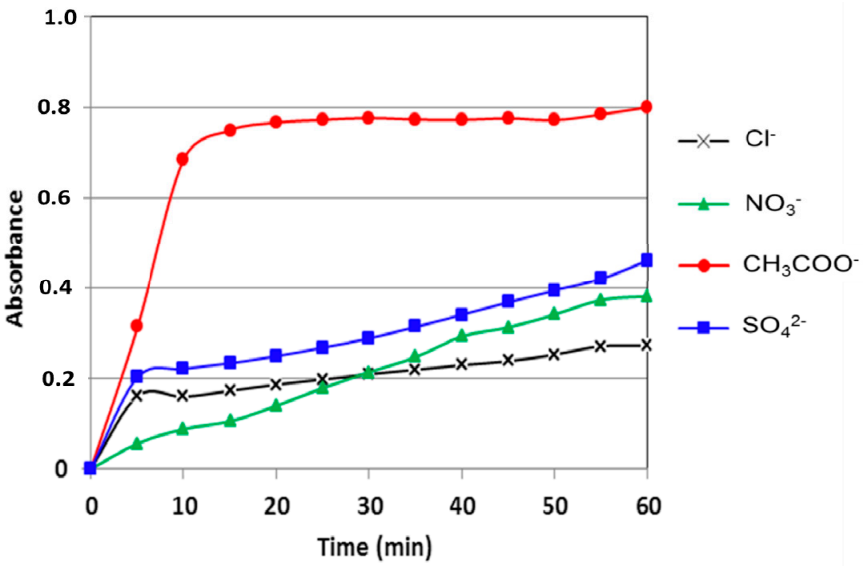


**Figure S3.** Catechol oxidation in the presence of copper complexes formed with **L**3**.**

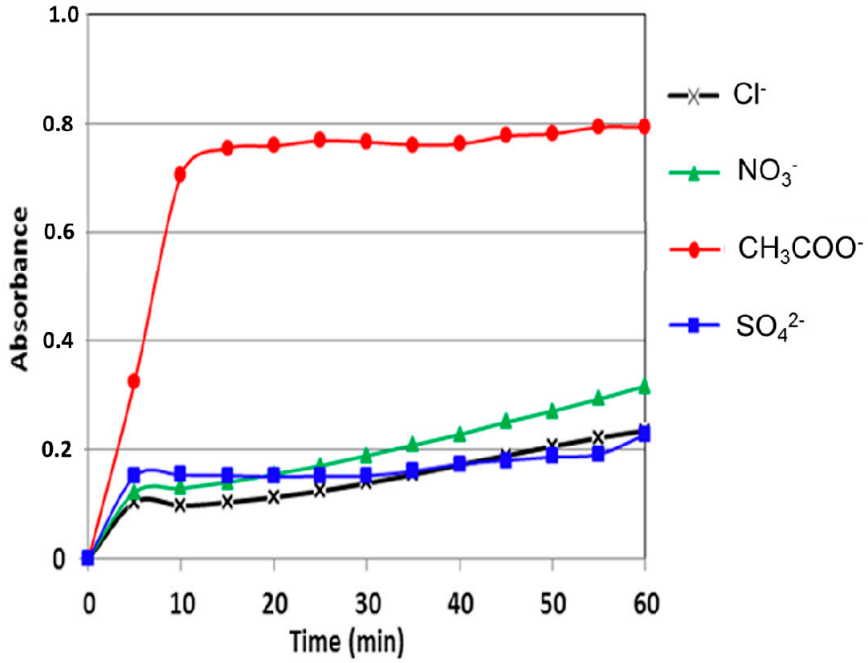


**Figure S4.** Catechol oxidation in the presence of copper complexes formed with **L**4**.**

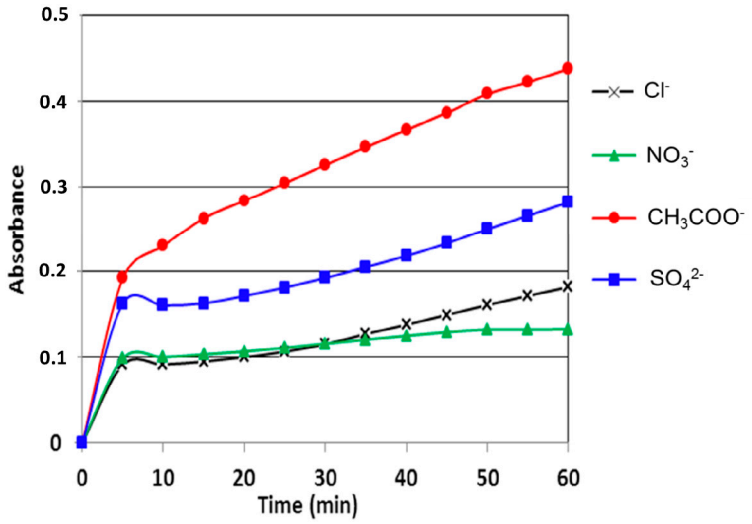


**Figure S5.** Catechol oxidation in the presence of copper complexes formed with **L5**.

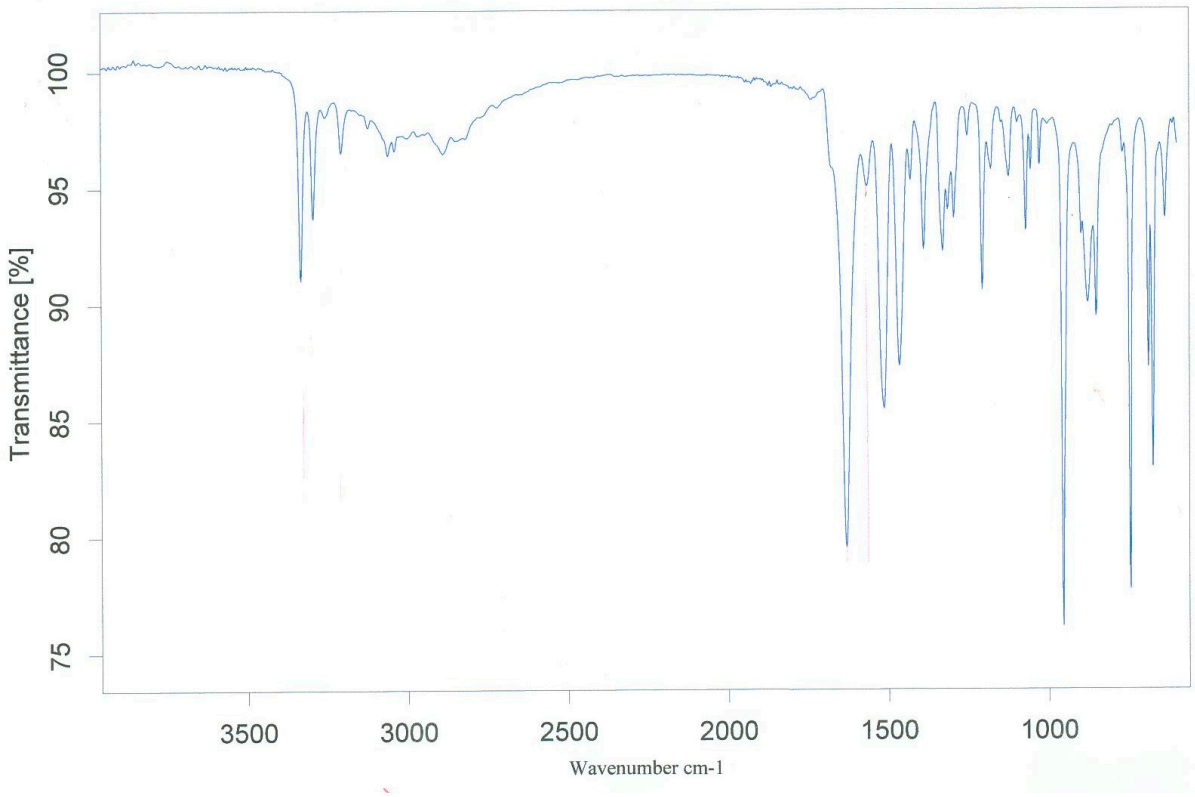


**Figure S6**. FT-IR spectrum of **2**.

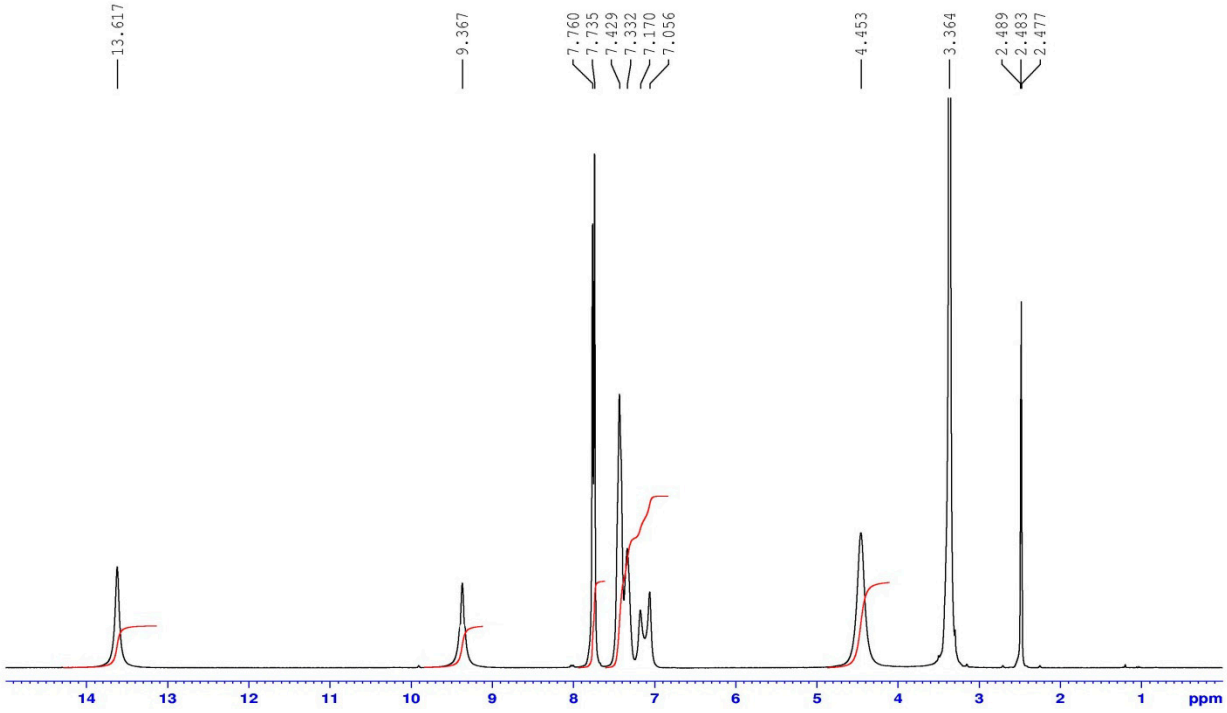


**Figure S7**. $^{1}$H NMR spectrum of **2**.

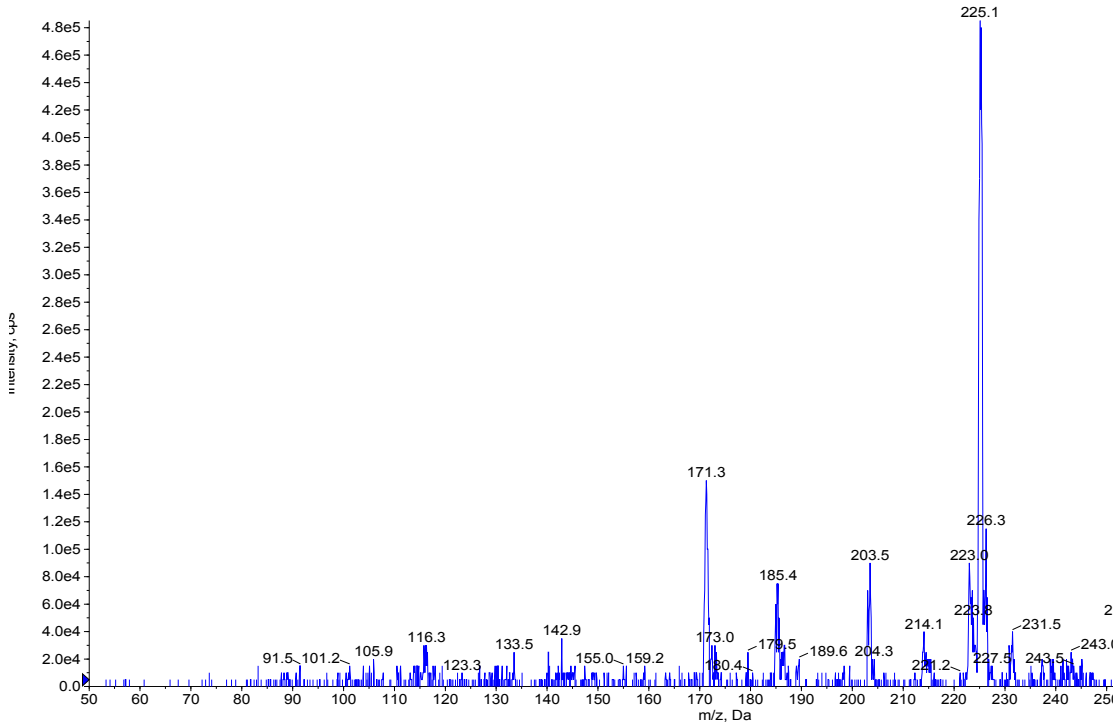


**Figure S8**. Mass spectrum of **2**.

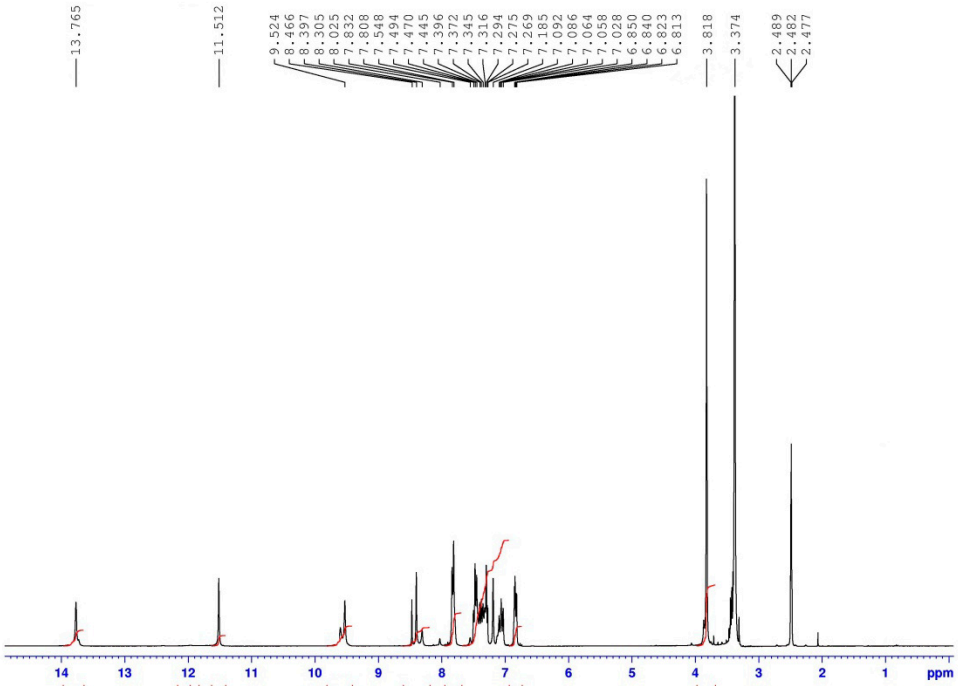


**Figure S9**. [1]H NMR spectrum of **L1**.

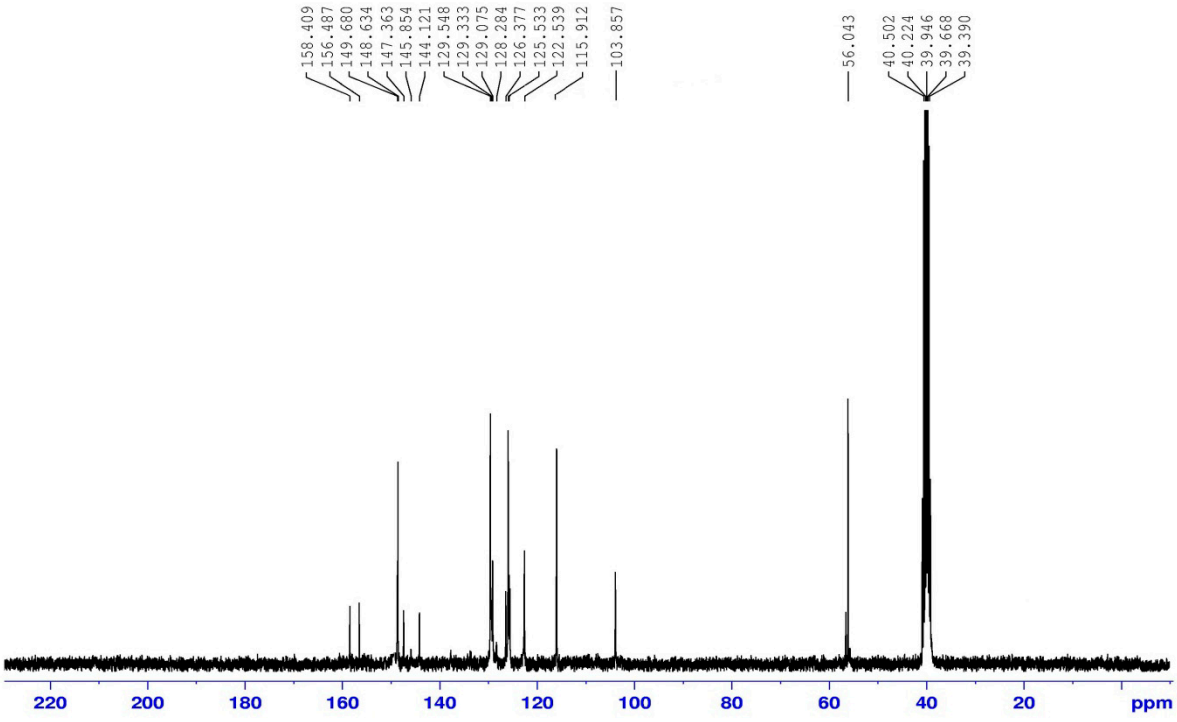


**Figure S10**. [13]C NMR spectrum of **L1**.

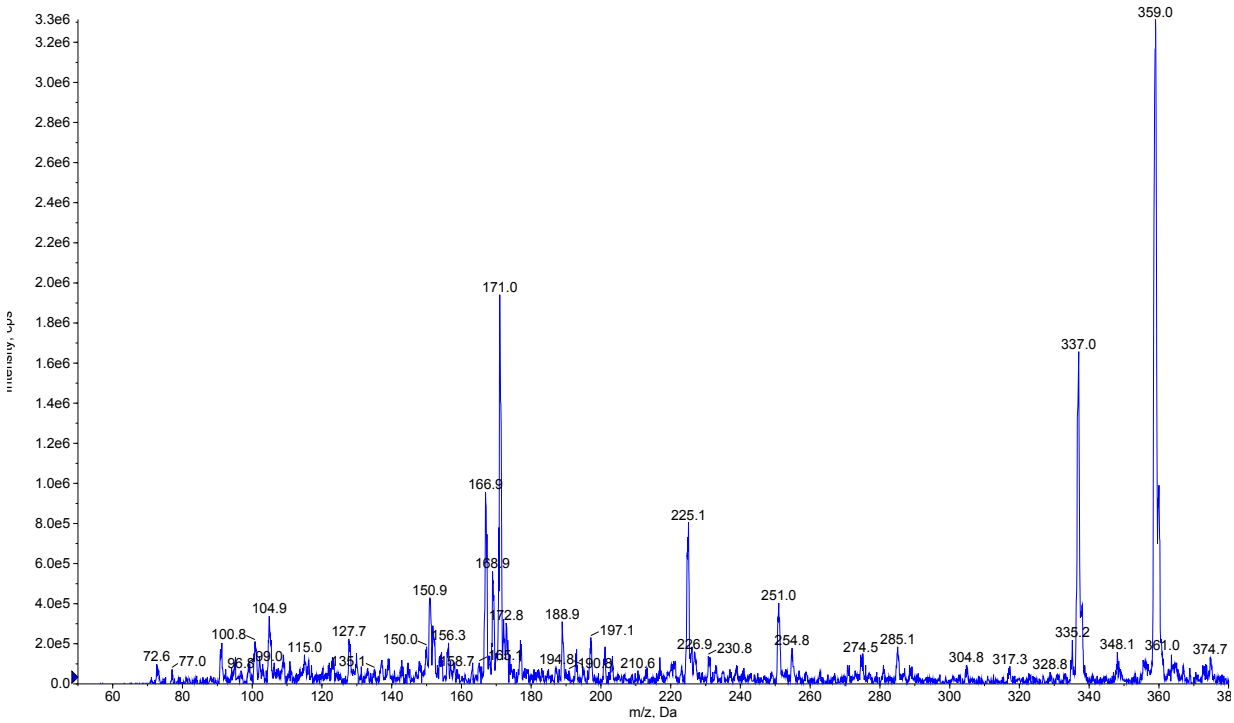


**Figure S11**. Mass spectrum of **L1**.

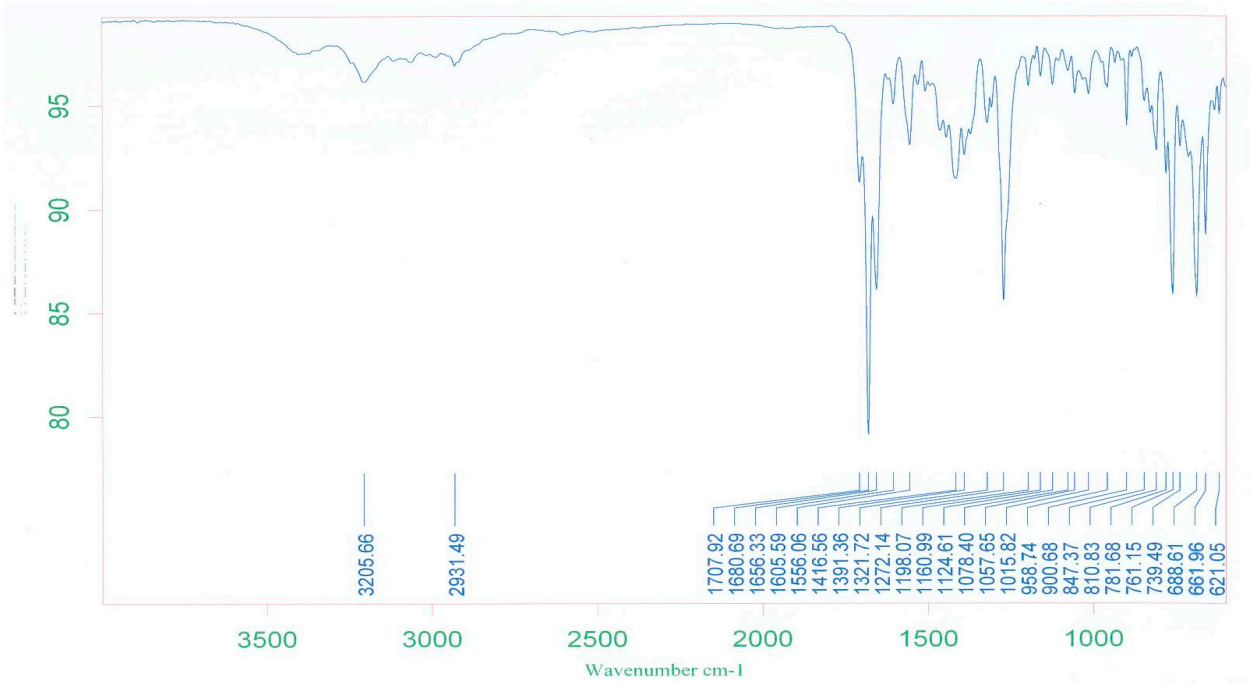


**Figure S12**. FT-IR spectrum of **L2**.

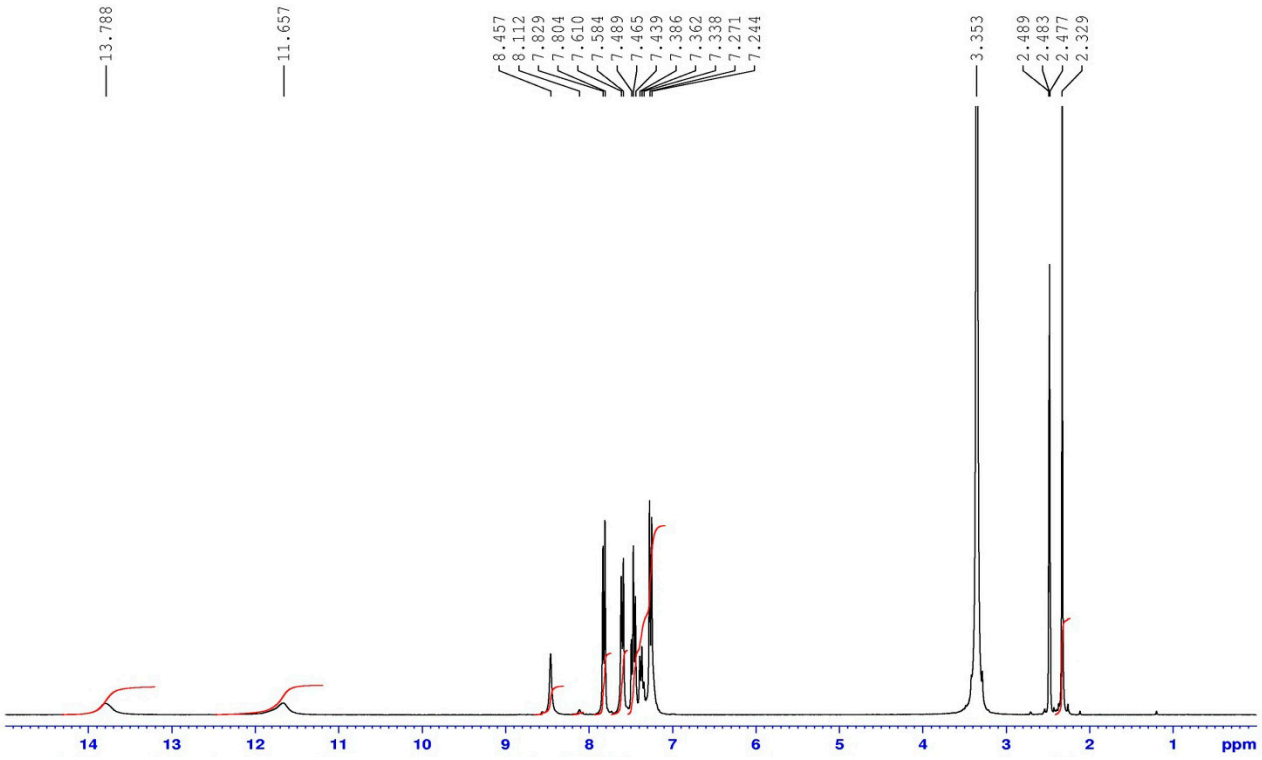


**Figure S13**. [1]H NMR spectrum of **L2**.

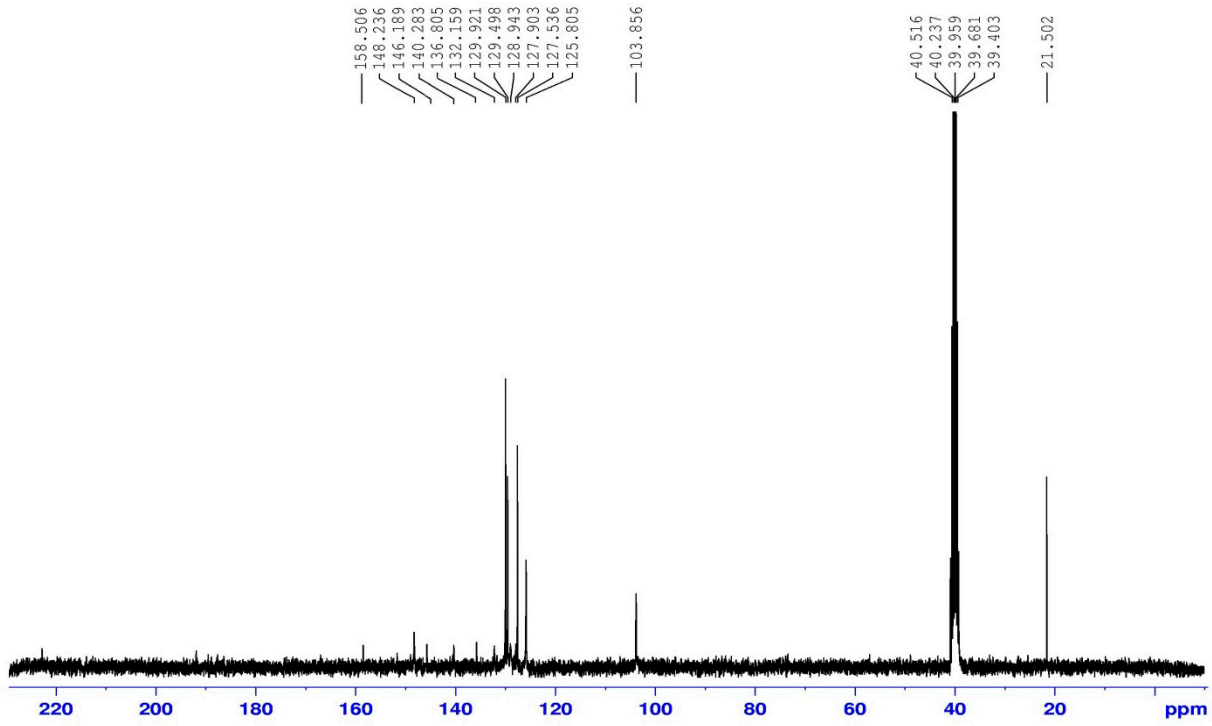


**Figure S14**. [13]C RMN spectrum of **L2**.

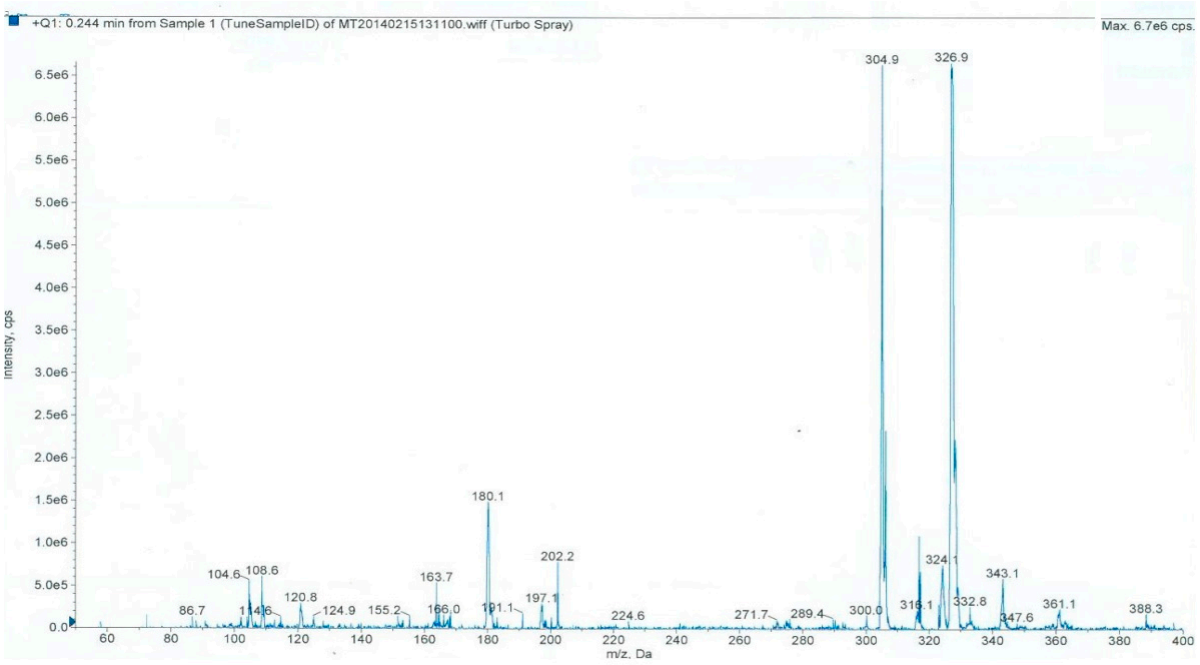


**Figure S15**. Mass spectrum of **L2**.

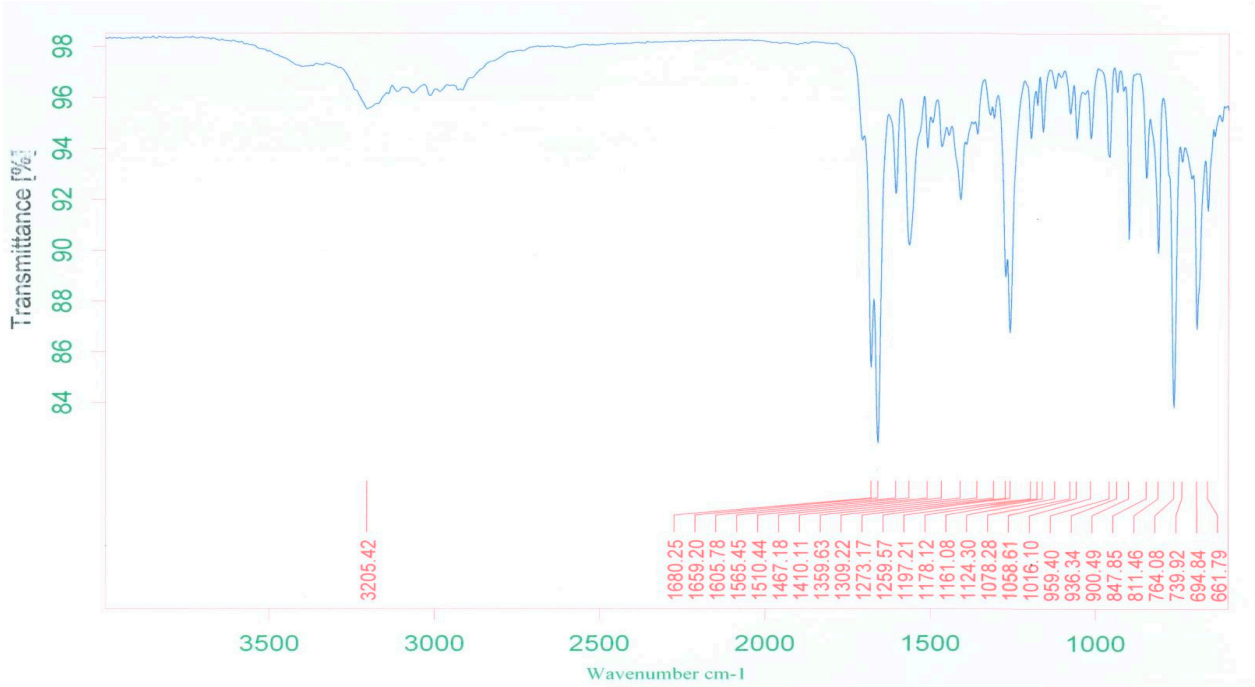


**Figure S16**. FT-IR spectrum of **L3**.

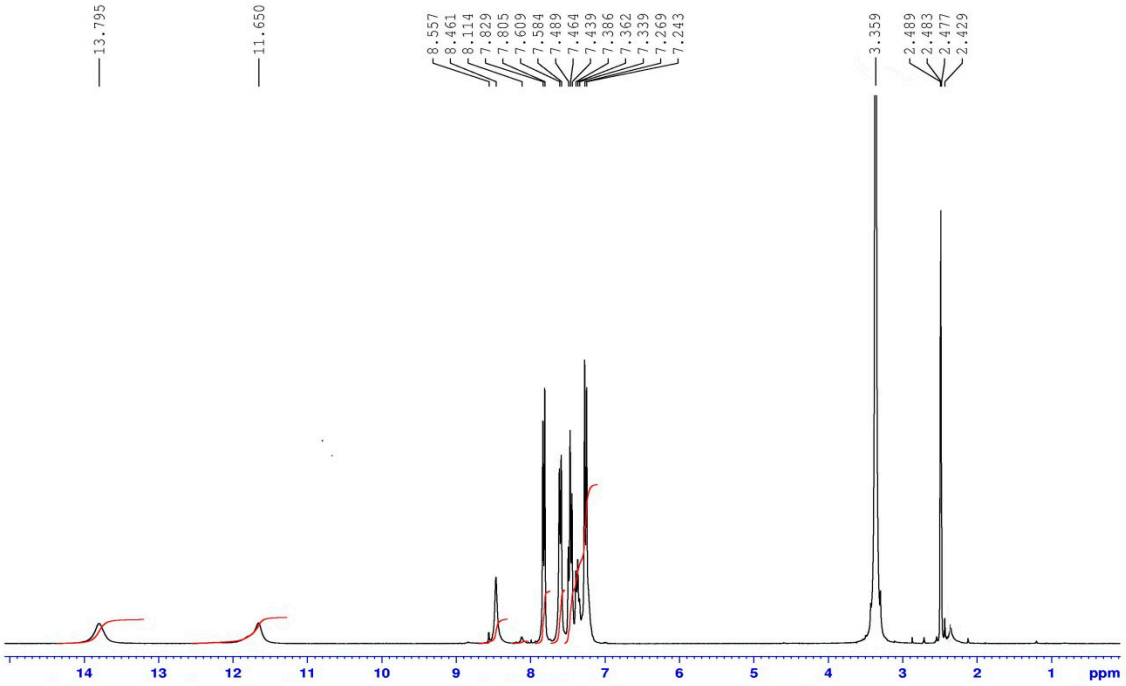


**Figure S17**. $^{1}$H NMR spectrum of **L3**.

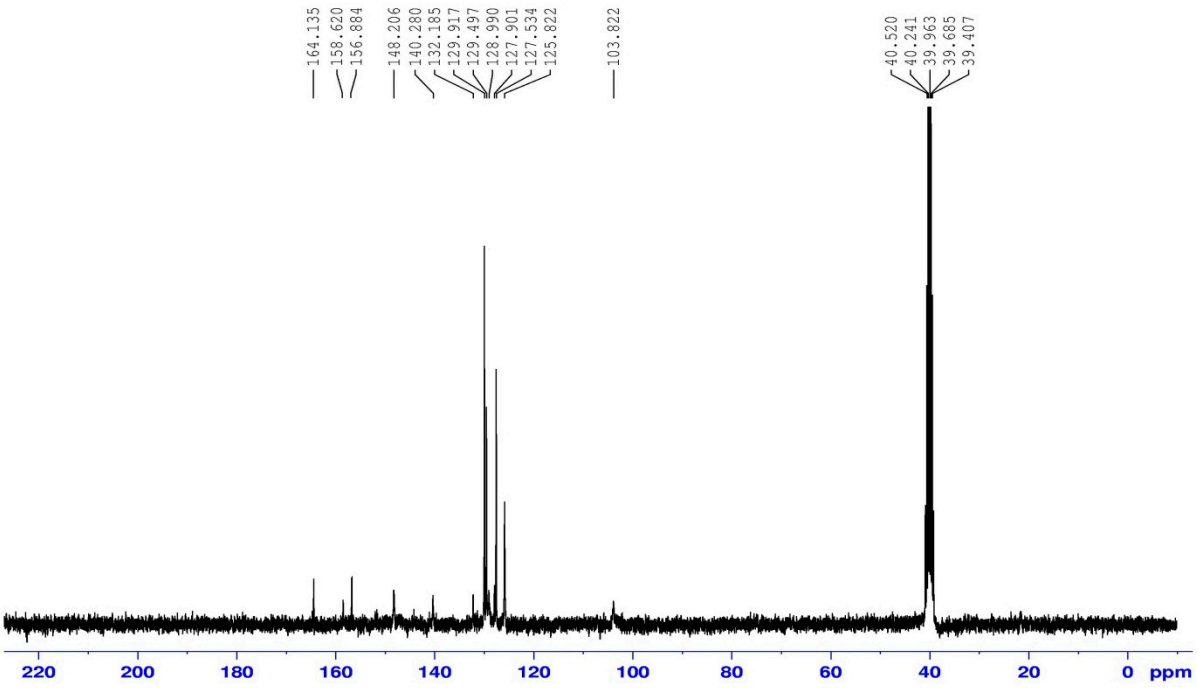


**Figure S18**. $^{13}$C NMR spectrum of **L3**.

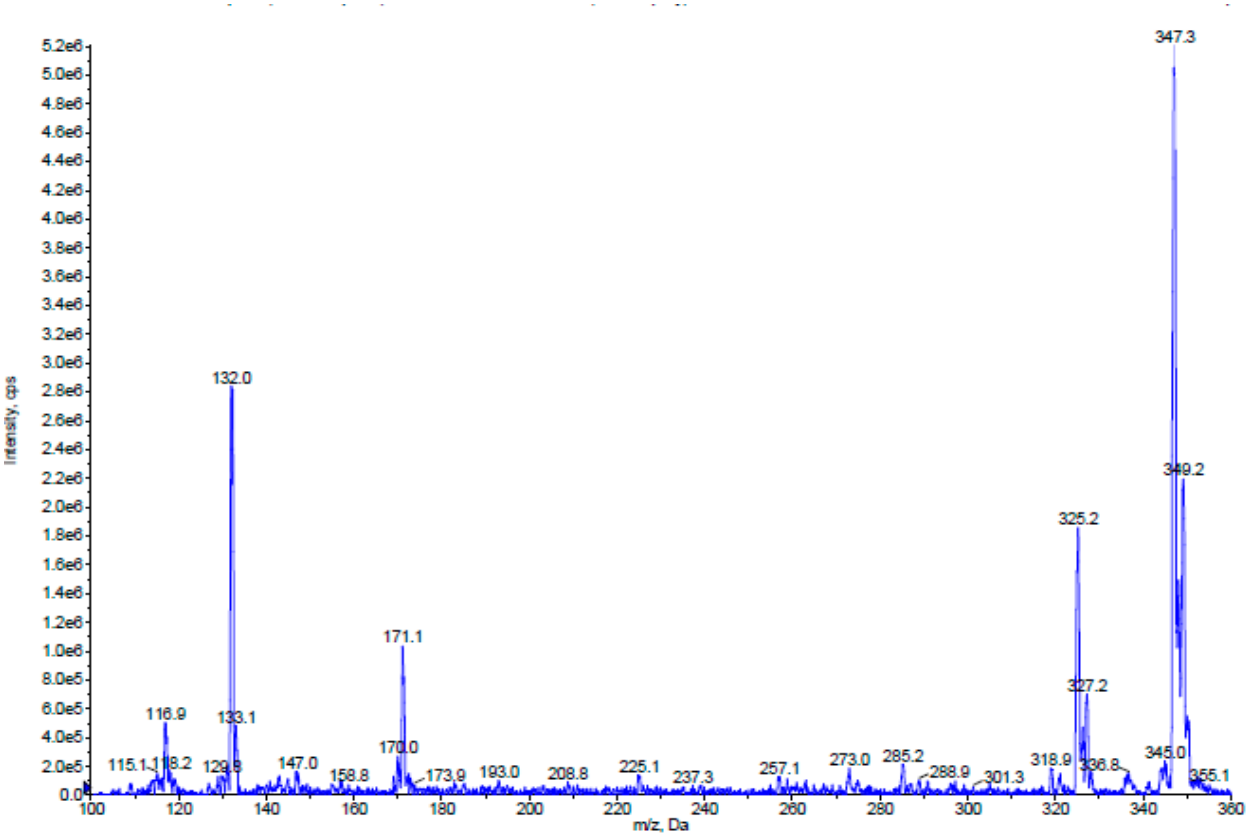


**Figure S19**. Mass spectrum of **L3**.

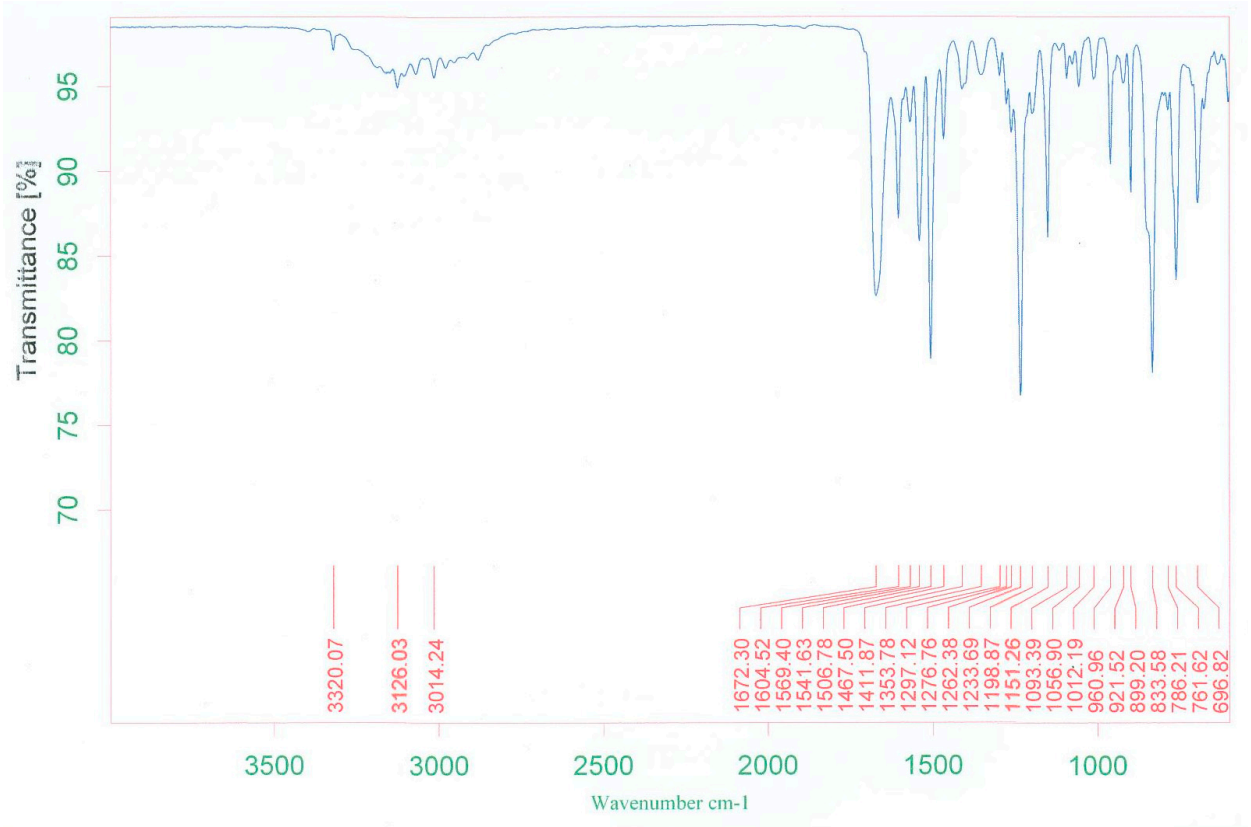


**Figure S20**. FT-IR spectrum of **L4**.

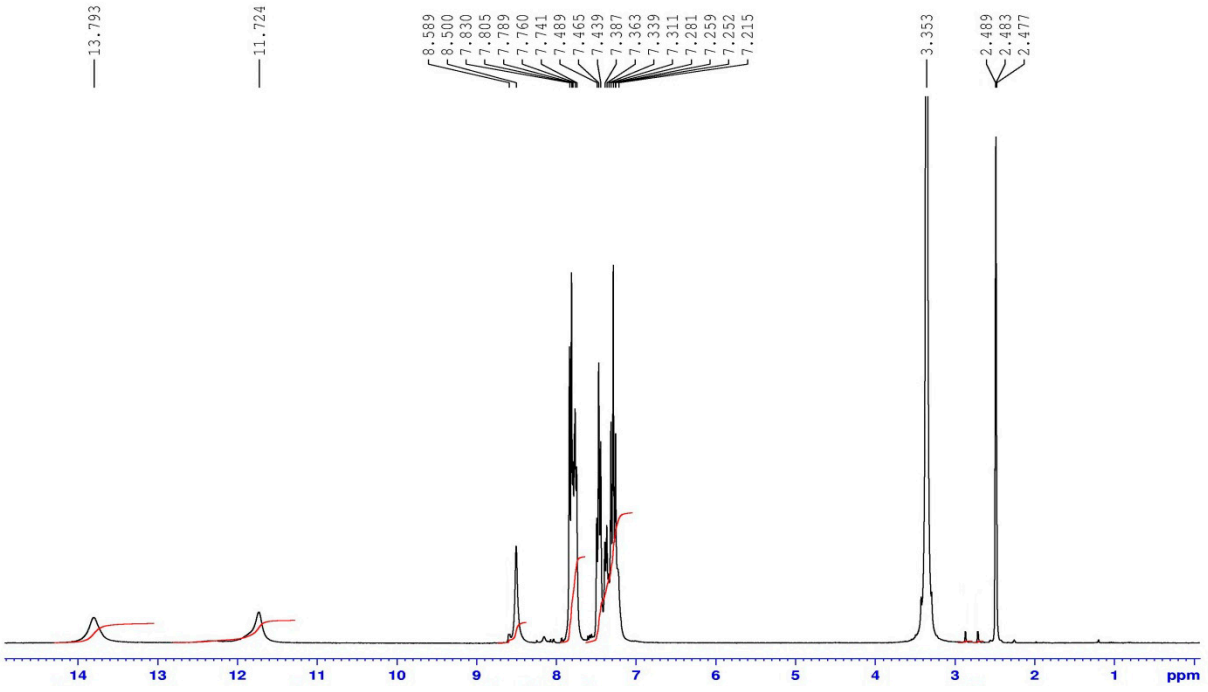


**Figure S21**. $^{1}$H NMR spectrum of **L4**.

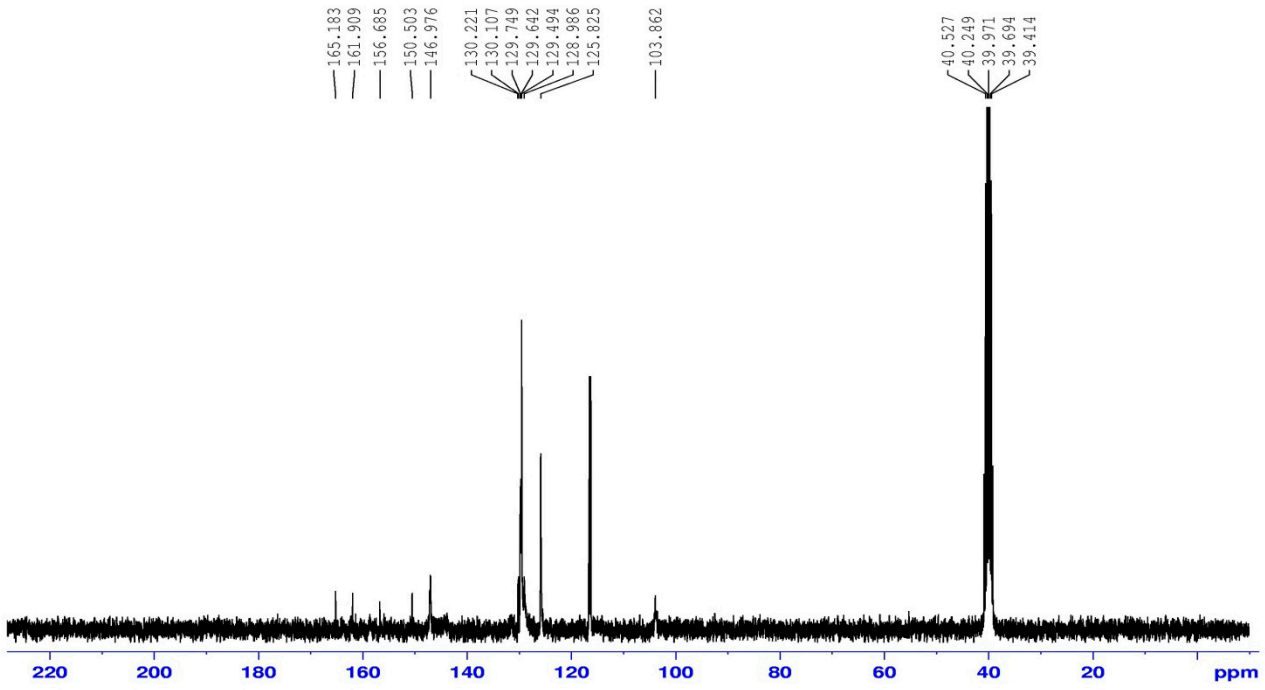


**Figure S22**. $^{13}$C NMR spectrum of **L4**.

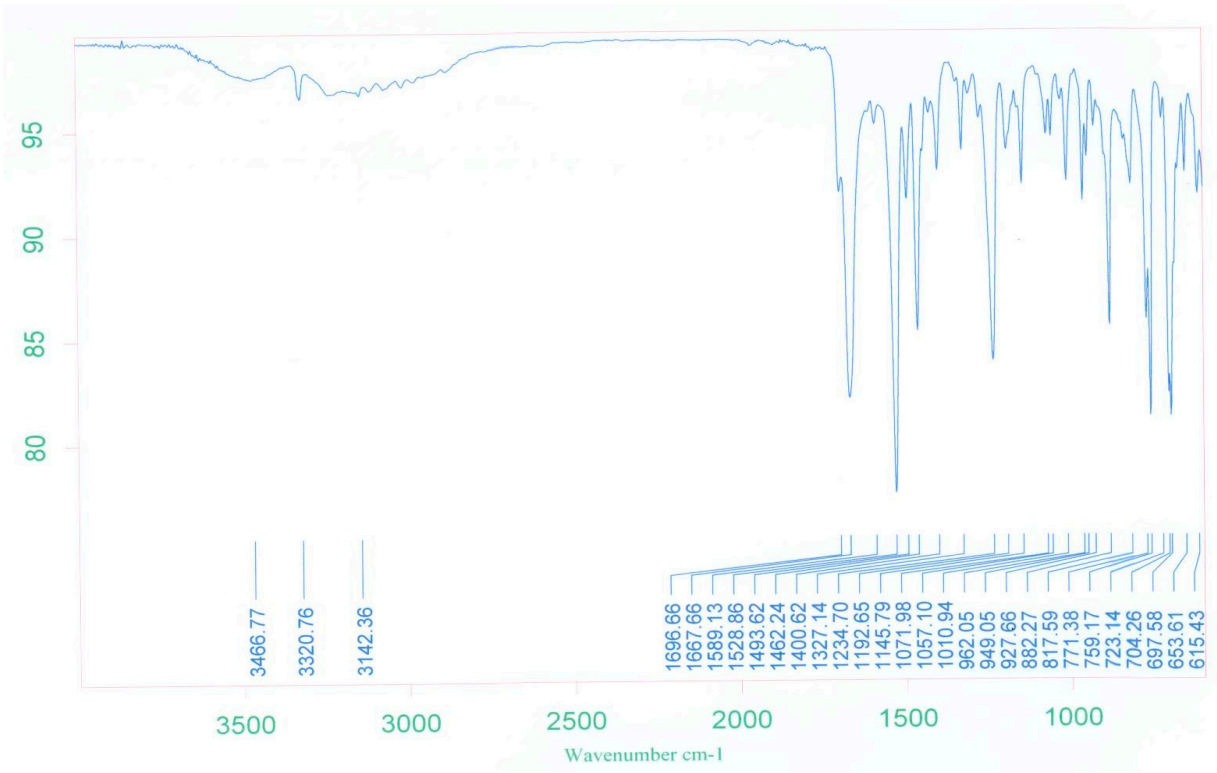


**Figure S23**. FT-IR spectrum of **L5**.

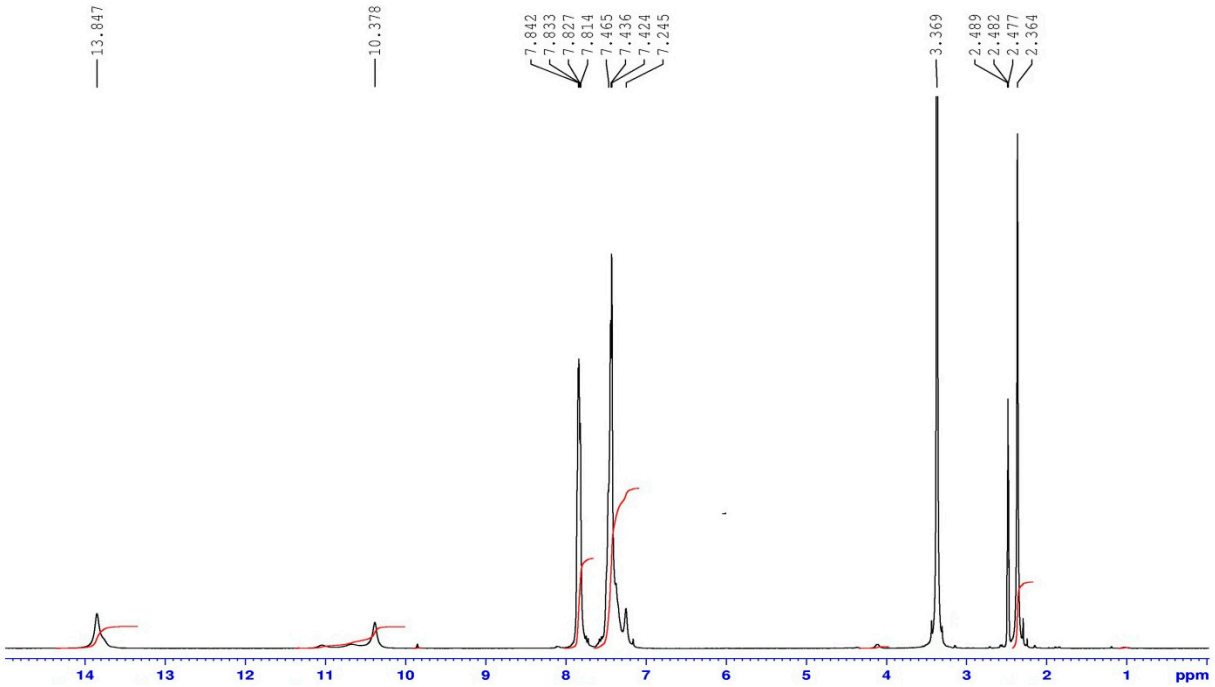


**Figure S24**. $^{1}$H NMR spectrum of **L5**.

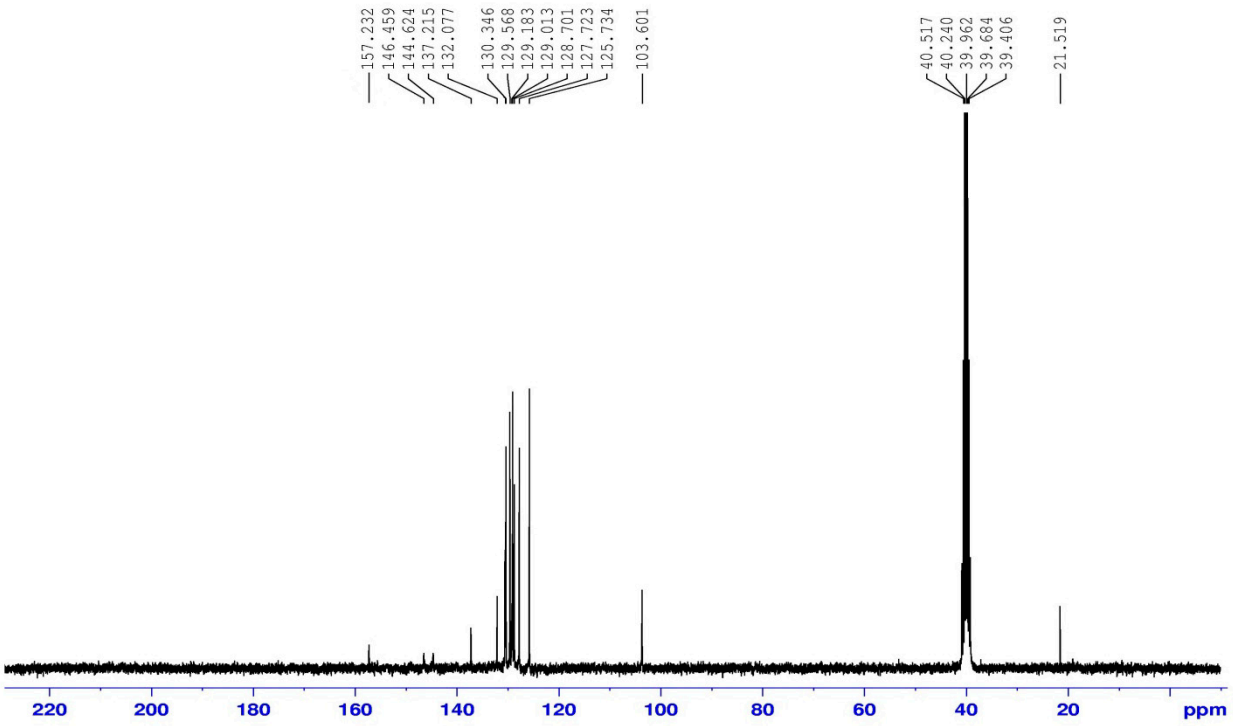


**Figure S25**. $^{13}C$ NMR spectrum of **L5**.

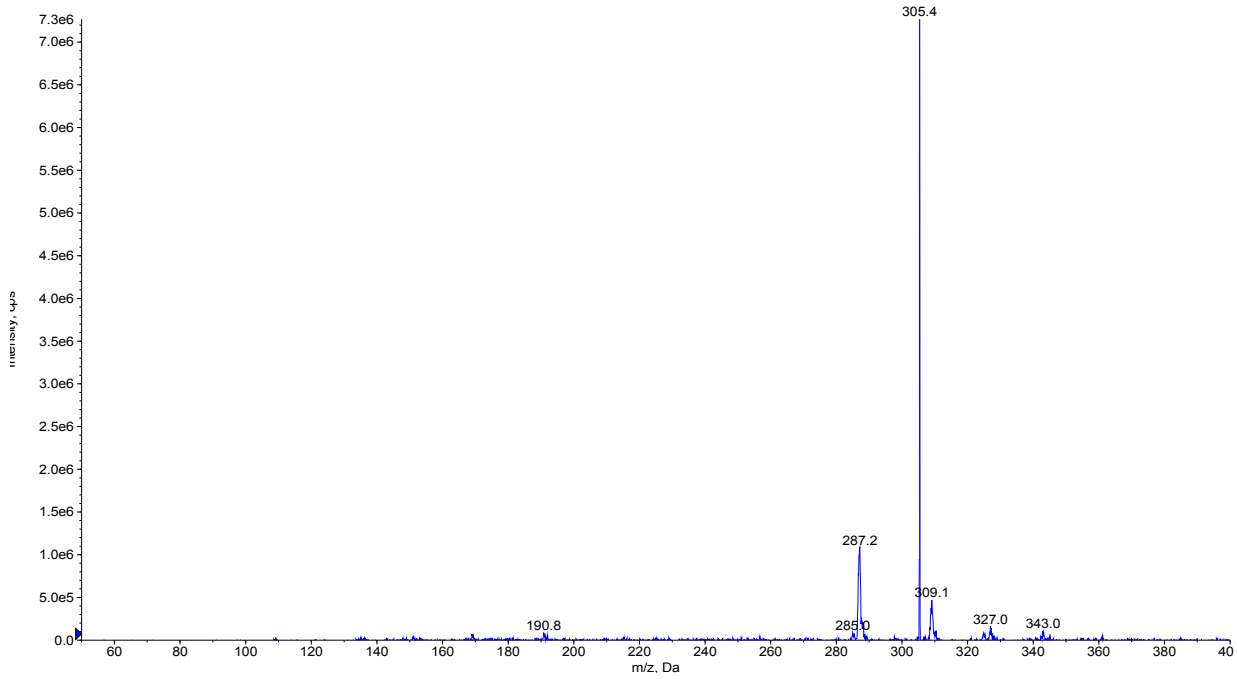


**Figure S26**. Mass spectrum of **L5**.

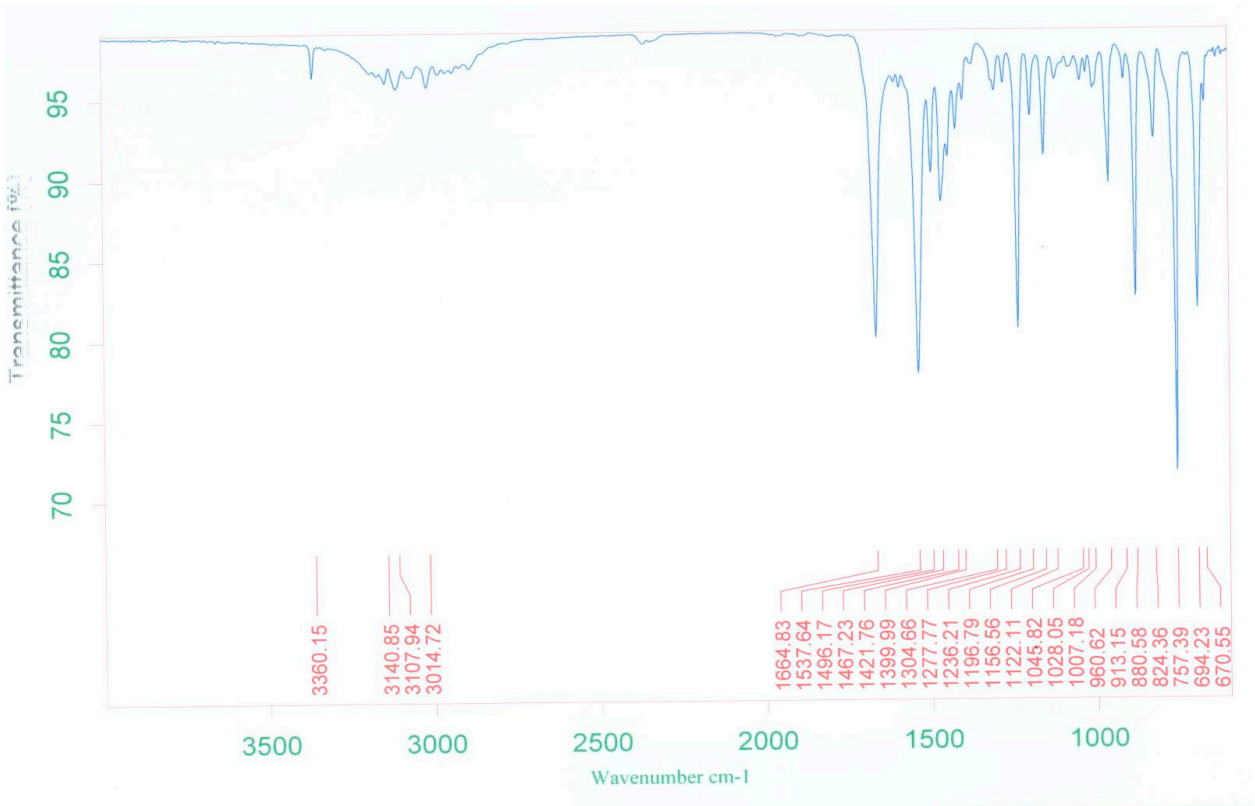


**Figure S27**. FT-IR spectrum of **L6**.

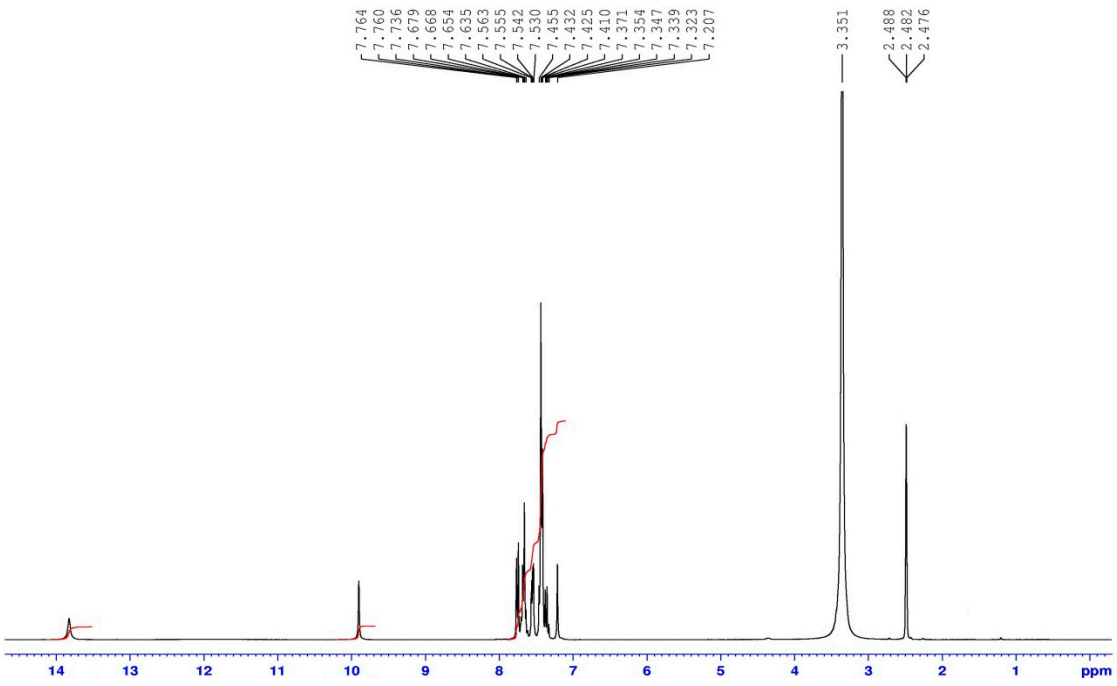


**Figure S28**. $^{1}$H NMR spectrum of **L6**.

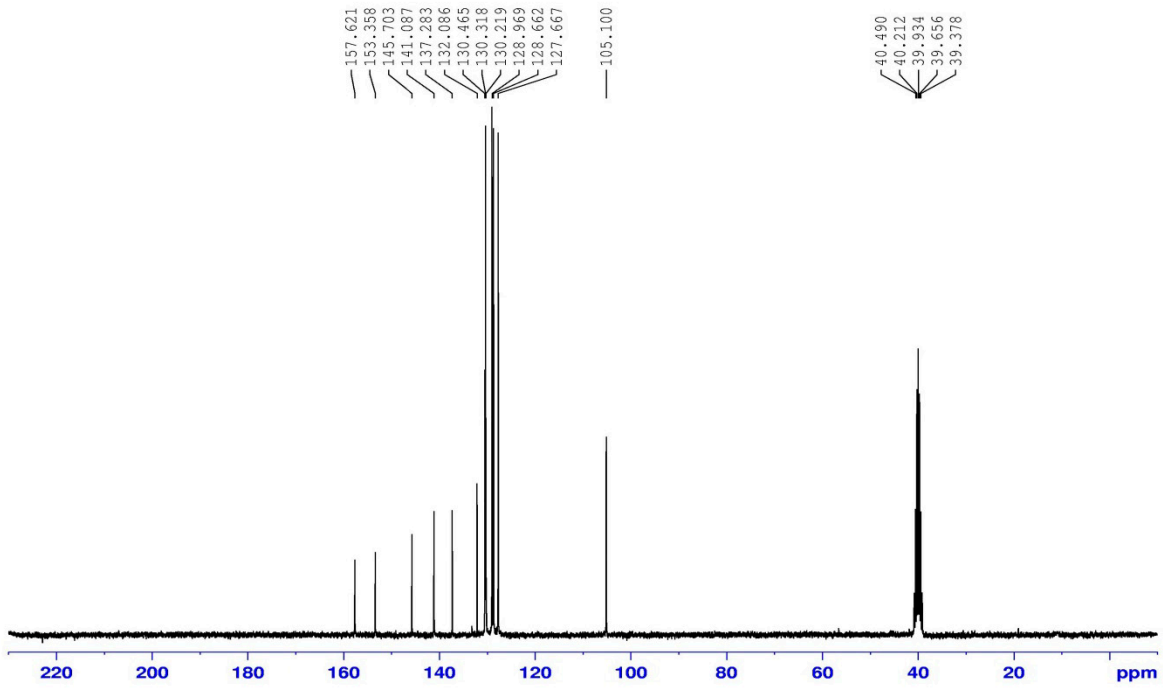


**Figure S29**. $^{13}C$ NMR spectrum of **L6**.

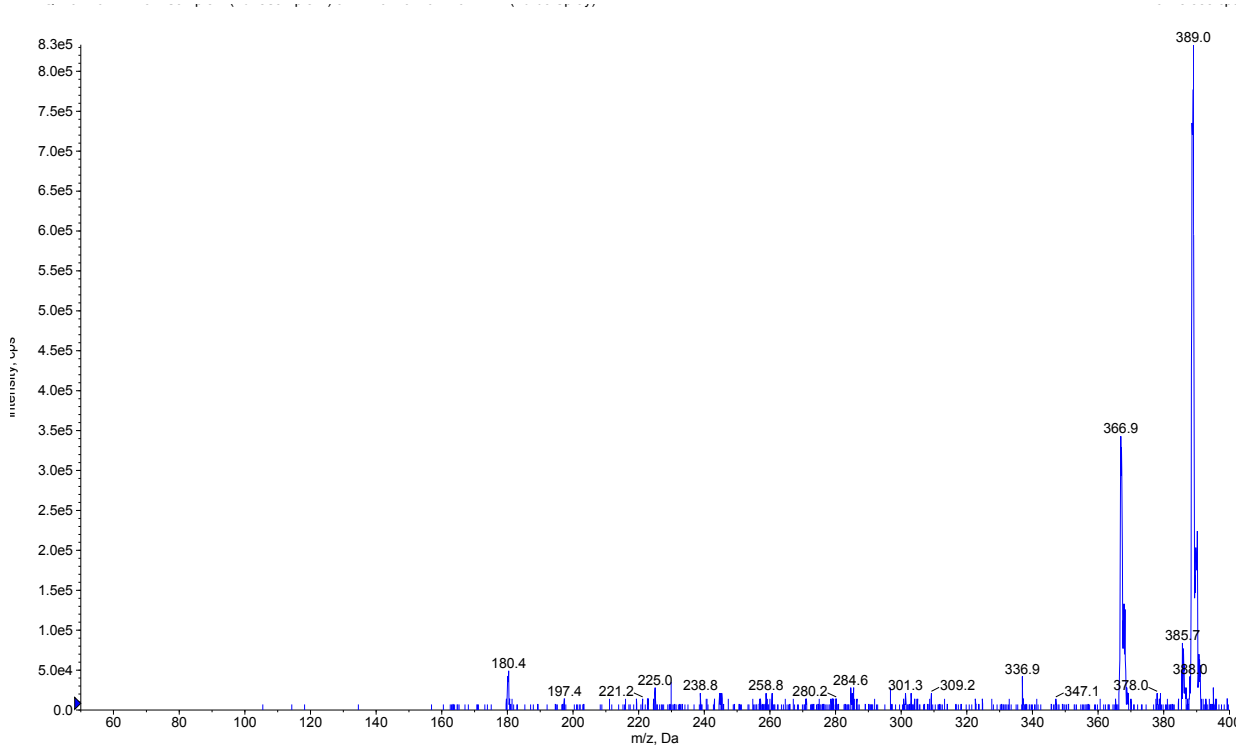


**Figure S30**. Mass spectrum of **L6**.