**Supporting Information**

Synthesis of Spirocyclic 5-7 Cycloheptenes by Rhodium Catalysed Chemo- and Regioselective [3+2+2] Cycloadditions

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**Experimental Section**

Unless otherwise noted, commercial available materials were used without further purification. Air sensitive reactions were carried out under argon atmosphere. Anhydrous solvents were obtained from Merck. Thin layer chromatography (TLC) was carried out using 0.2 mm Kieselgel F254 (Merck) silica plates and compounds visualized in para-anisaldehyde strain. NMR spectra were recorded on a Bruker 300 MHz spectrometer operating at 300 MHz for 1H and 75 MHz for 13C. Chemical shifts (*δ*) are quoted in parts per million (ppm) relative to internal solvent reference (CDCl3; *δ* = 7.26 for 1H NMR and *δ* = 77.0 for 13C NMR). Coupling constants are given in Hz and chemical shifts are reported in *δ* values in ppm. Data are reported as followed: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, dd = double doublet, m = multiplet), coupling constants (Hz), and integration. High resolution mass spectra were recorded on a Brucker-micrOTOF-Q II mass spec-trometer.

**General procedure for synthesis of [3+2+2] cycloadducts (3a-f):** To a solution of **1** (1 *equiv.*) in toluene (3ml), alkynes **2** (10 *equiv.*) was added and reaction mixture was degassed for 10 minutes under argon atmosphere. This is followed by the addition [Rh(COD)Cl]2 (0.1 *equiv.*) and triphenylphosphite (0.25 *equiv.*). The reaction was heated at 110-130 °C for 20-30 hrs depending on type of alkynes. After completion of reaction, the reaction mixture was concentrated under high vacuum at 35-40 °C to get crude product. Crude product was purified using silica gel (100-200 mesh) column chromatography and 20% ether in hexane as eluent to get compound **3**.

*Trimethyl 8-methylene-1,3,3a,7,8,8a-hexahydro-2H-spiro[azulene-4,1'-cyclopropane]-2,2,6-tricarboxylate*, **3a**: Colourless liquid; yield: 41%;1H NMR (300 MHz, CDCl3): *δ* 6.34 (s, 1H), 4.81 (dd, *J* = 7.5, 2.1 Hz, 2H), 3.98 (s, 3H), 3.94 (s, 3H), 3.72 (s, 3H), 3.26 (t, *J* = 17.7 Hz, 2H), 3.07 (dd, *J* = 17.7, 9 Hz,1H), 2.58-2.66 (m, 1H), 2.30 (dd, *J* = 6.9, 1.5 Hz,1H), 2.11- 2.20 (m, 2H), 1.56-1.64 (m, 1H), 0.65-0.80 (m, 4H); 13C NMR (75 MHz, CDCl3): δ 172.7, 172.1, 167.9, 147.5, 134.6, 131.1, 114.2, 59.5, 52.8, 52.6, 51.9, 50.5, 46.6, 38.6, 38.2, 34.0, 20.3, 17.6, 14.9; LRMS 349.2 (M+1), HRMS calcd for C19H25O6 (MH+): 349.1651, found: 349.1639.

*6-Ethyl 2,2-di-methyl 5-methyl-8-methylene-1,3,3a,7,8,8a-hexahydro-2H-spiro[azulene-4,1'-cyclopropane]-2,2,6-tricarboxylate,* **3b**: Colourless liquid; yield: 32%; 1H NMR (300 MHz, CDCl3): *δ* 4.83 (dd, *J* = 7.5, 2.1 Hz, 2H), 4.19 (q, *J* = 7.5 Hz, 2H), 3.97 (s, 6H),3.26 (t, *J* = 18.0 Hz, 2H), 3.12 (dd, *J* = 18.0, 9 Hz,1H), 2.58-2.64 (m, 1H), 2.30 (dd, *J* = 6.9, 1.2 Hz,1H), 2.12- 2.17 (m, 2H), 1.82 (s, 3H), 1.57-1.65 (m, 1H), 1.32 (t, *J* = 7.5 Hz, 3H ) 0.66-0.81 (m, 4H); 13C NMR (75 MHz, CDCl3): *δ* 172.5, 172.2, 168.0, 148.3, 147.3, 131.3, 114.2, 61.2, 59.5, 52.8, 52.3, 50.2, 46.6, 38.7, 38.3, 34.2, 20.5, 17.6, 14.9, 14.0, 12.2; LRMS 377.2 (M+1). HRMS calcd for C21H29O6 (MH+): 377.1964, found: 377.1959.

*6-Ethyl 2,2-dimethyl 5-ethyl-8-methylene-1,3,3a,7,8,8a-hexahydro-2H-spiro[azulene-4,1'-cyclopropane]-2,2,6-tricarboxylate,* **3c**: Pale yellow liquid; yield:35%;1H NMR (300 MHz, CDCl3): *δ* 4.81 (dd, *J* = 7.2, 2.1 Hz, 2H), 4.21 (q, *J* = 7.5 Hz, 2H), 3.95 (s, 6H), 3.26 (t, *J* = 17.7 Hz, 2H), 3.08 (dd, *J* = 17.7, 9.3 Hz,1H), 2.58-2.66 (m, 1H), 2.30 (dd, *J* = 6.9, 1.5 Hz,1H), 2.13- 2.18 (m, 2H), 2.01 (q, *J* = 7.2 Hz, 2H), 1.59-1.66 (m, 1H), 1.30 (t, *J* = 7.5 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H), 0.65-0.83 (m, 4H); 13C NMR (75 MHz, CDCl3): *δ* 172.7, 172.1, 167.8, 148.5, 147.5, 131.3, 114.4, 61.4, 59.7, 52.6, 52.3, 50.3, 46.6, 38.8, 38.2, 34.3, 20.5, 19.5, 17.7, 15.1, 14.1, 12.9; LRMS 391.3 (M+1), HRMS calcd for C22H31O6(MH+): 391.2121, found: 391.2125.

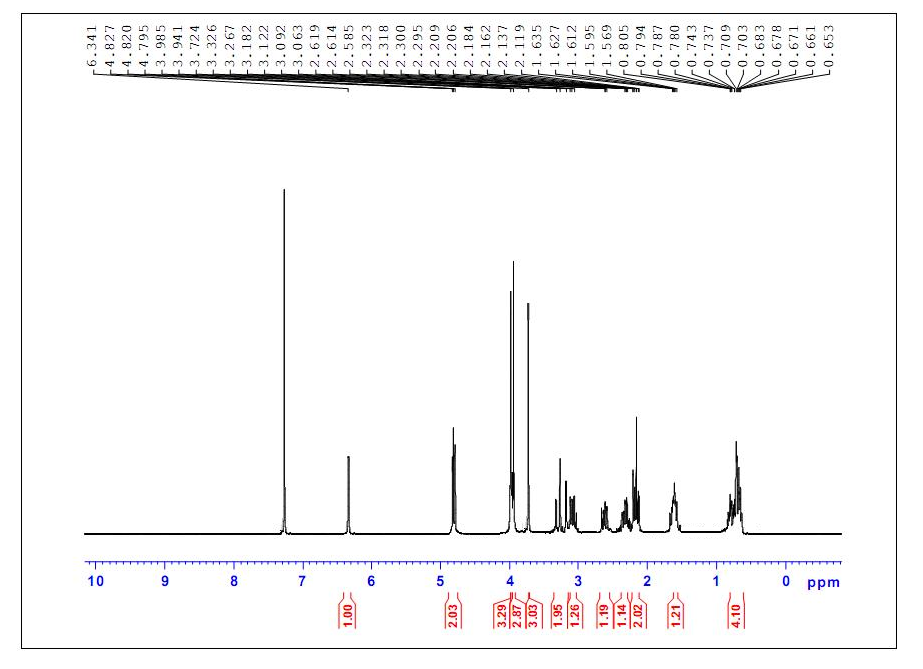
*6-Ethyl 2,2-methyl 8-methylene-5-phenyl-1,3,3a,7,8,8a-hexahydro-2H-spiro[azulene-4,1'-cyclopropane]-2,2,6-tricarboxylate,* **3d**: Colourless liquid; yield: 36%;1H NMR (300 MHz, CDCl3): *δ* 7.20-7.35 (m, 5H), 4.81 (dd, *J* = 7.5, 2.4 Hz, 2H), 4.21 (q, *J* = 7.5 Hz, 2H), 3.99 (s, 6H), 3.28 (t, *J* = 18.0 Hz, 2H), 3.10 (dd, *J* = 18.0, 9 Hz,1H), 2.60-2.63 (m, 1H), 2.32 (dd, *J* = 6.9, 1.2 Hz,1H), 2.10- 2.19 (m, 2H), 1.58-1.62 (m, 1H), 1.31 (t, *J* = 7.5 Hz, 3H) 0.69-0.81 (m, 4H); 13C NMR (75 MHz, CDCl3): *δ* 172.5, 172.2, 168.0, 150.1, 147.4, 139.4, 131.1, 129.2, 128.7, 128.3, 127.0, 113.9, 61.1, 59.7, 52.8, 52.3, 50.3, 46.6, 38.7, 38.0, 34.1, 20.4, 17.7, 15.0, 14.1; LRMS 439.2 (M+1), HRMS calcd for C26H31O6 (MH+): 439.2121, found: 439.2129.

*2,2-Diethyl 6-methyl 8-methylene-1,3,3a,7,8,8a-hexahydro-2H-spiro[azulene-4,1'-cyclopropane]-2,2,6-tricarboxylate,* **3e**: Colourless liquid; yield: 44%; 1H NMR (300 MHz, CDCl3): *δ* 6.32 (s, 1H), 4.80 (dd, *J* = 9, 2.1 Hz, 2H), 4.16 (qd, *J* = 6.9, 2.1 Hz,4H), 3.73 (s, 3H), 3.26 (t, *J* = 17.7 Hz, 2H), 3.08 (dd, *J* = 17.7, 9 Hz,1H), 2.57-2.60 (m, 1H), 2.29 (dd, *J* = 7.2, 1.5 Hz,1H), 2.10- 2.19 (m, 2H), 1.58-1.65 (m, 1H), 1.24 (t, *J* = 2.1 Hz,6H), 0.64-0.83 (m, 4H); 13C NMR (75 MHz, CDCl3): *δ* 172.6, 171.9, 168.0, 147.7, 134.5, 131.1, 114.4, 61.3, 59.9, 52.0, 50.6, 46.8, 38.6, 38.3, 34.1, 20.4, 17.6, 15.0, 14.1; LRMS 377.1 (M+1), HRMS calcd for C21H29O6 (MH+): 377.1964, found: 377.1951.

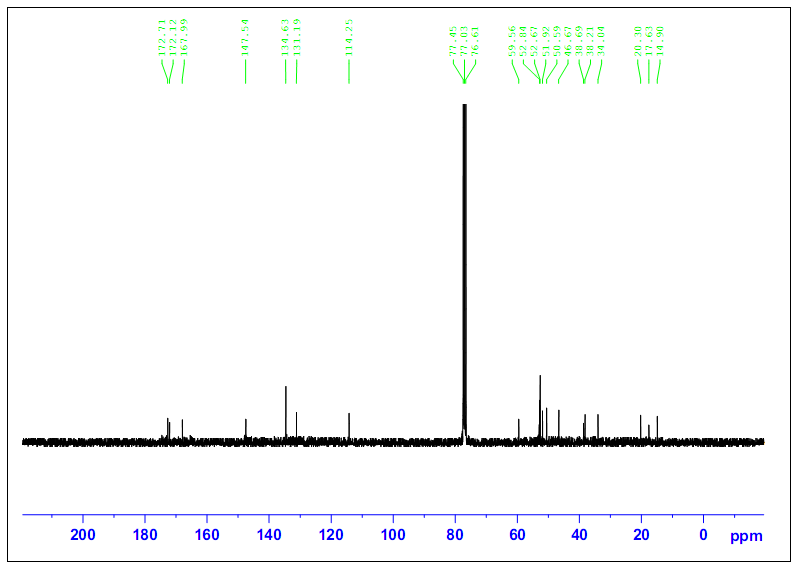
*2,2-Diisopropyl 6-methyl 8-methylene-1,3,3a,7,8,8a-hexahydro-2H-spiro[azulene-4,1'-cyclopropane]-2,2,6-tricarboxylate,* **3f**: Colourless liquid; yield: 46%; 1H NMR (300 MHz, CDCl3): *δ* 6.34 (s, 1H), 5.06 (m, 2H), 4.81 (dd, *J* = 10.2, 2.1 Hz, 2H), 3.73 (s, 3H), 3.28 (t, *J* = 18 Hz, 2H), 3.10 (dd, *J*= 18, 9.6 Hz, 1H), 2.56-2.62 (m, 1H), 2.25-2.30 (m, 1H), 2.09- 2.18 (m, 2H), 1.60-1.65 (m, 1H), 1.22 (d, *J* = 6.3 Hz, 12H), 0.65-0.80 (m, 4H); 13C NMR (75 MHz, CDCl3): *δ* 172.7, 172.0, 167.8, 147.5, 134.5, 131.3, 114.2, 68.5, 60.1, 51.8, 50.7, 46.8, 38.4, 38.1, 34.2, 21.7, 20.3, 17.7, 15.0; LRMS 405.3 (M+1), HRMS calcd for C23H33O6 (MH+): 405.2277, found: 405.2281.

**Characterization data:**

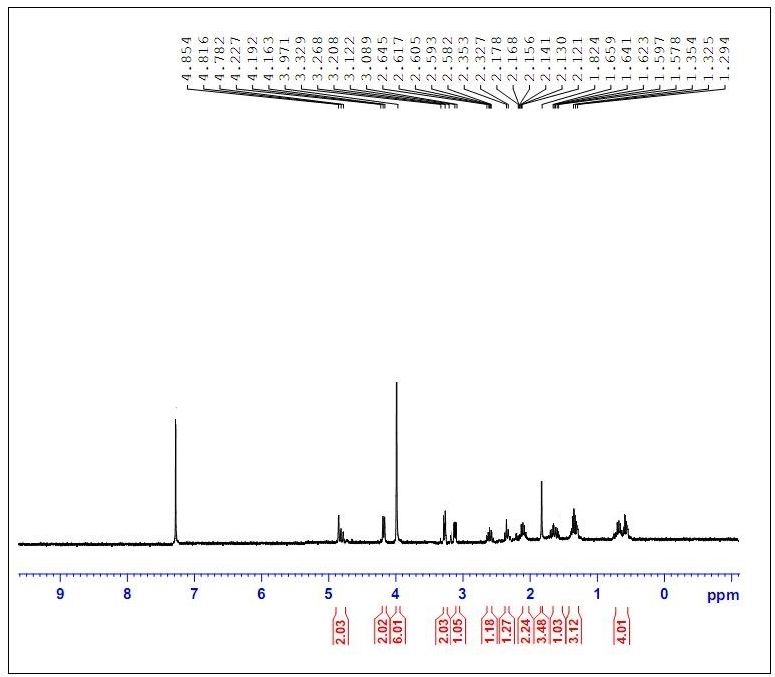
1H NMR AND 13C NMR SPECTRA



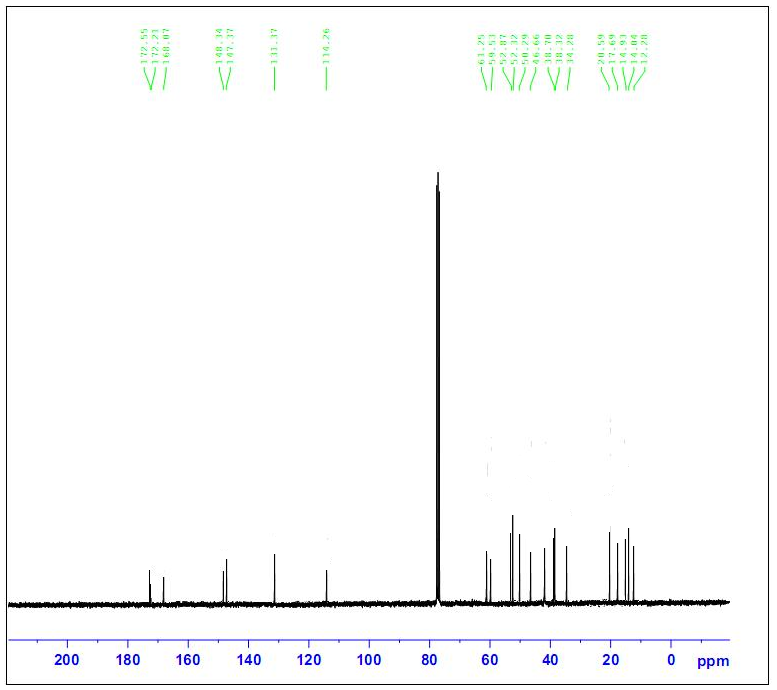
**Figure S 1**. 1H NMR (300 MHz, CDCl3) of **3a**

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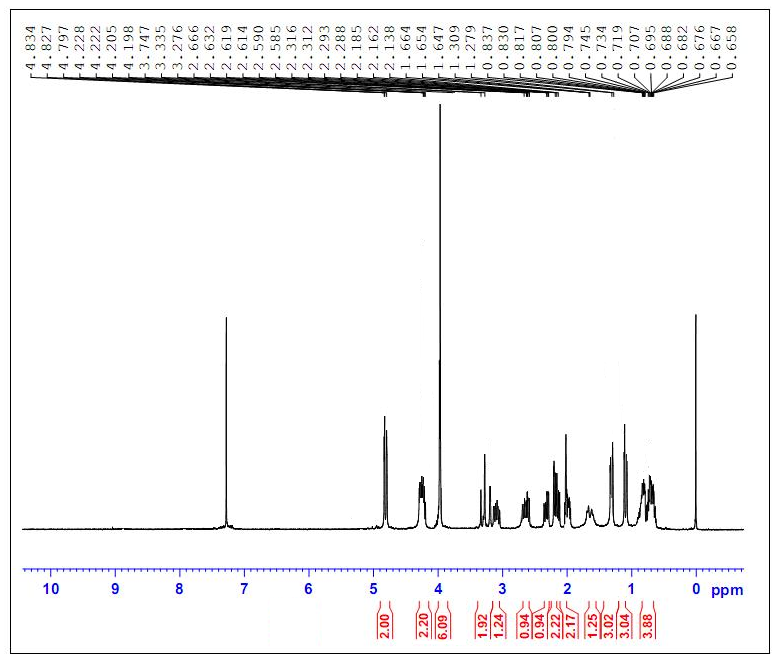
**Figure S 2**. 13C NMR (75 MHz, CDCl3) of **3a**

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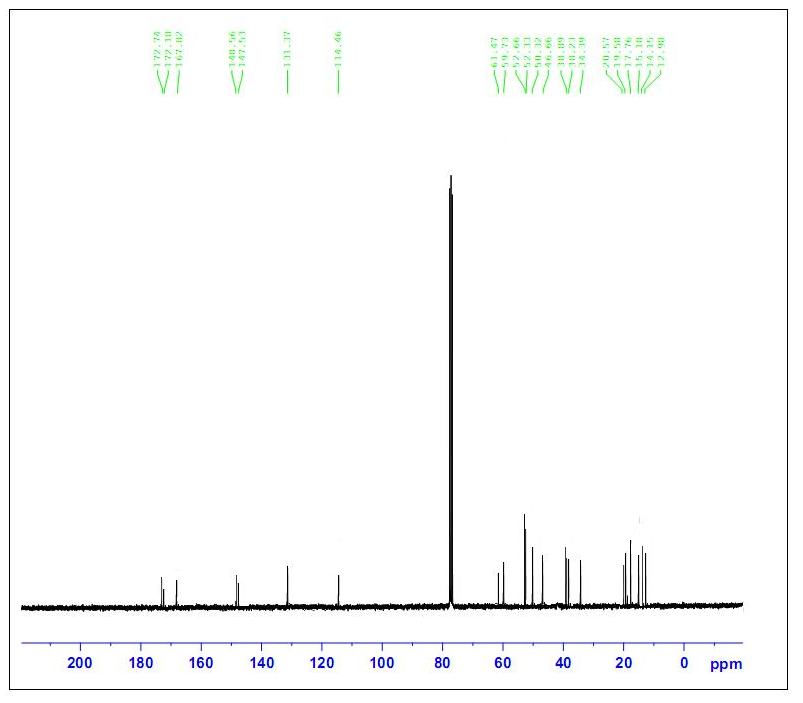
**Figure S 3**. 1H NMR (300 MHz, CDCl3) of **3b**

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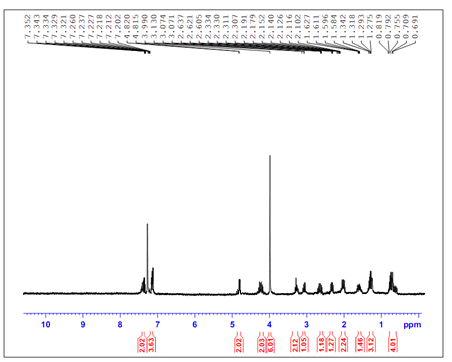
**Figure S 4**. 13C NMR (75 MHz, CDCl3) of **3b**

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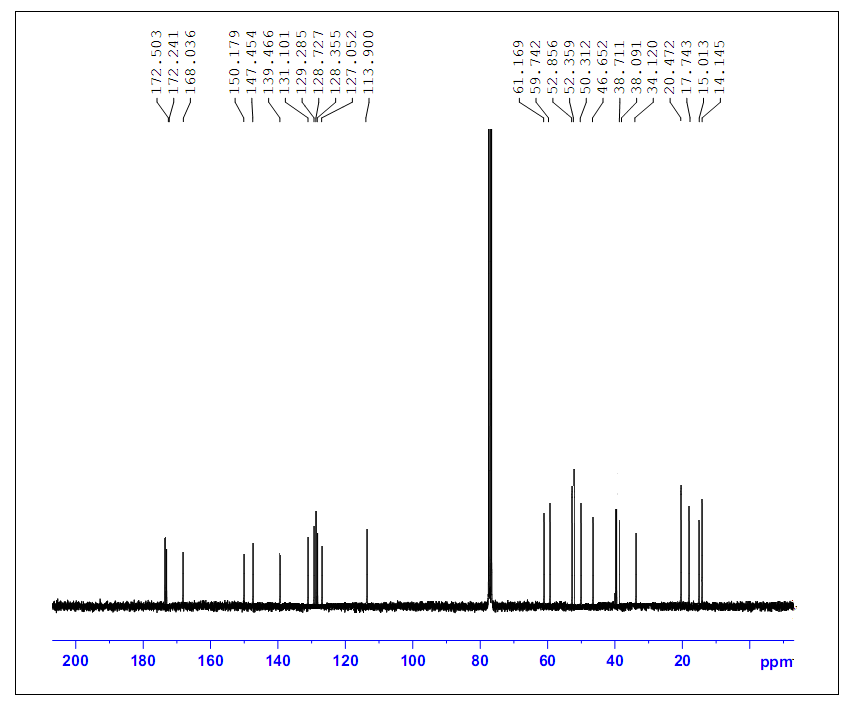
**Figure S 5**. 1H NMR (300 MHz, CDCl3) of **3c**

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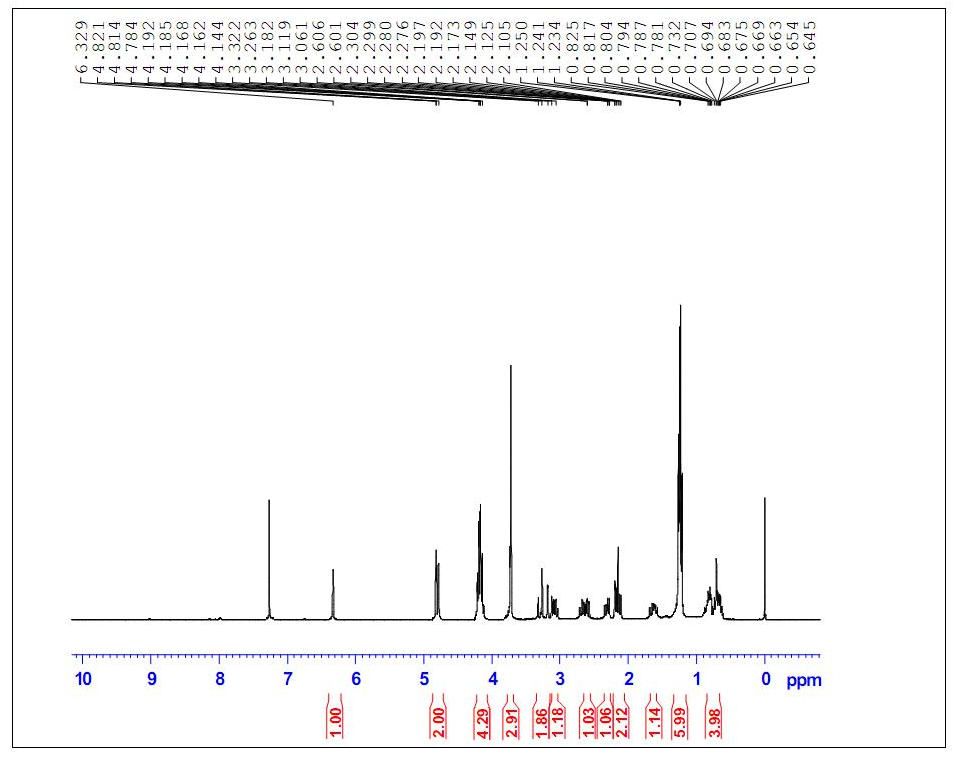
**Figure S 6**. 13C NMR (75 MHz, CDCl3) of **3c**

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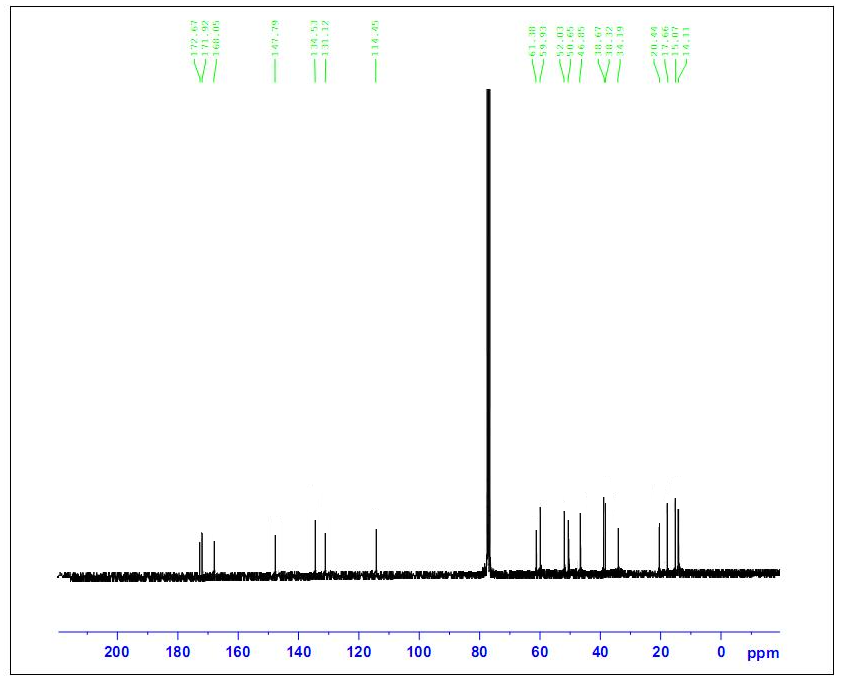
**Figure S 7**. 1H NMR (300 MHz, CDCl3) of **3d**

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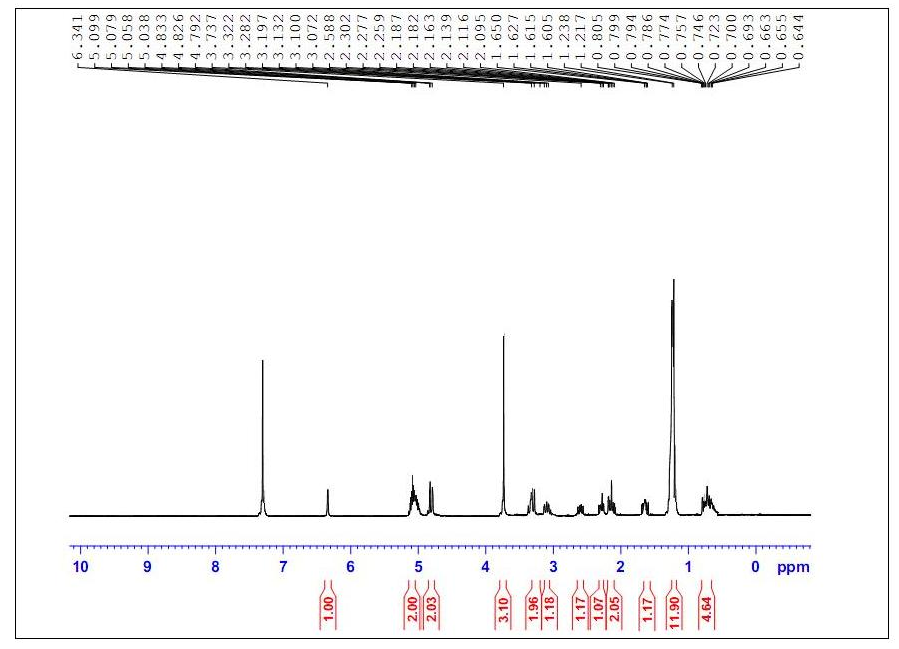
**Figure S 8**. 13C NMR (75 MHz, CDCl3) of **3d**

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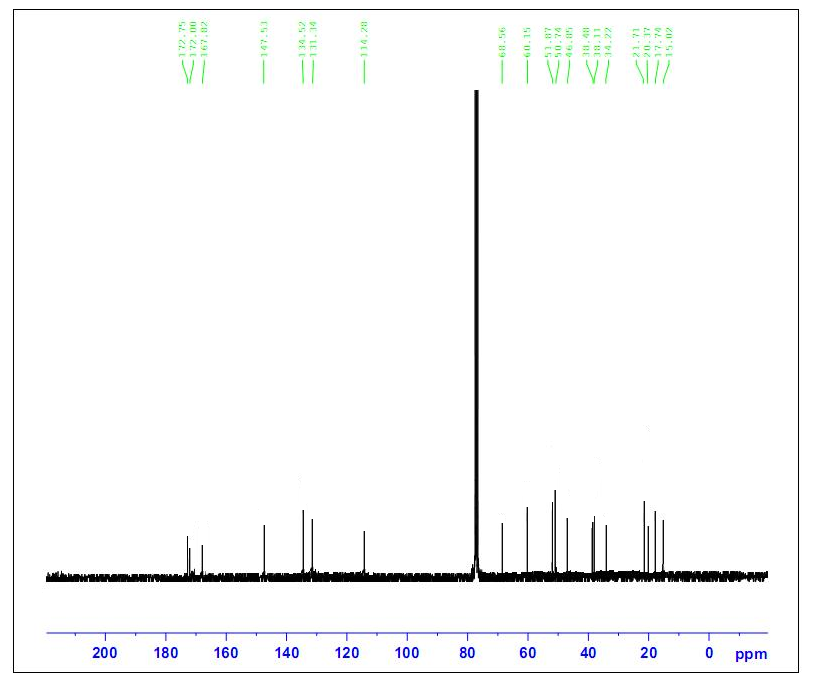
**Figure S 9**. 1H NMR (300 MHz, CDCl3) of **3e**

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**Figure S 10**. 13C NMR (75 MHz, CDCl3) of **3e**

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**Figure S 11**. 1H NMR (300 MHz, CDCl3) of **3f**

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**Figure S 12**. 13C NMR (75 MHz, CDCl3) of **3f**

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