

Aryl Acyl Peroxides for Visible-light Induced Decarboxylative Arylation of Quinoxalin-2(1*H*)-ones under Additive-, External Photosensitizer-free and Ambient Conditions

Long-Yong Xie^a, Sha Peng^a, Li-Hua Yang^a, Cun Peng^a, Ying-Wu Lin^c, Xianyong Yu^d, Zhong Cao^b, Yu-Yu Peng^b and Wei-Min He^{*a}

^aDepartment of Chemistry, Hunan University of Science and Engineering, Yongzhou 425100, China

^bHunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation, Changsha University of Science and Technology, Changsha, 410114, China

^cSchool of Chemistry and Chemical Engineering, University of South China, Hengyang 421001, China

^dSchool of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China

weiminhe2016@yeah.net

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1. General Information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz by using a Bruker Avance 400 spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (^1H NMR: CDCl_3 7.26 ppm, d^6 -DMSO 2.50 ppm, ^{13}C NMR: CDCl_3 77.0 ppm, d^6 -DMSO 40.0 ppm), the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad. Mass spectra were performed on a spectrometer operating on ESI-TOF. Column chromatography was performed on silica gel (200-300 mesh).

The Light Source and the Material of the Irradiation Vessel

Manufacturer: Beijin Rogertech Ltd.

Model: RLH-18

Broadband source: $\lambda = 415\text{-}420\text{ nm}$

Light intensity: 62.77185 mW/cm^2

Emission spectrum (figure S1):

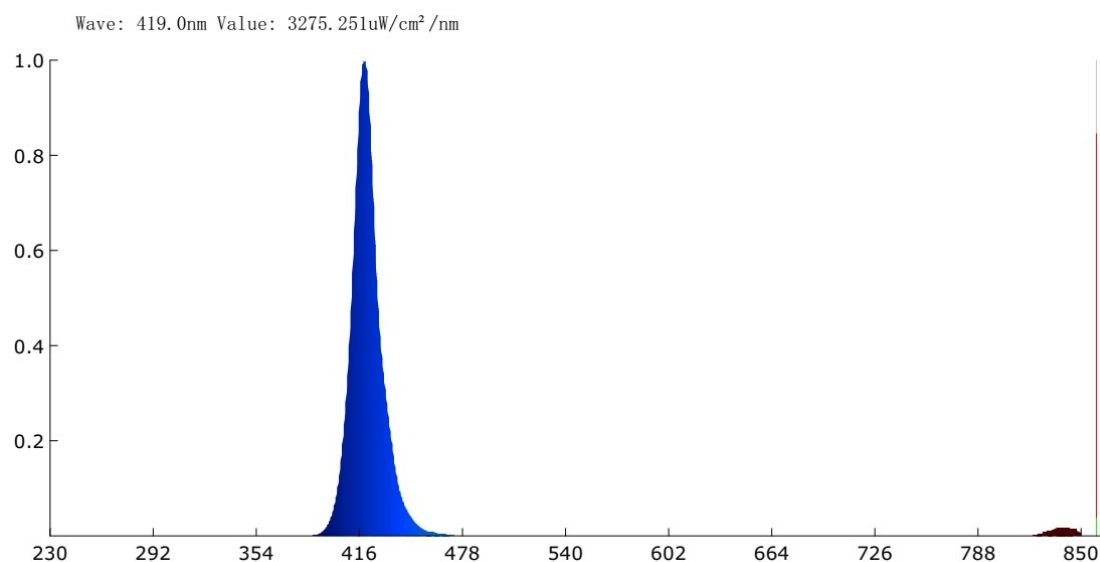


Figure S1

Material of the irradiation vessel: quartz tube

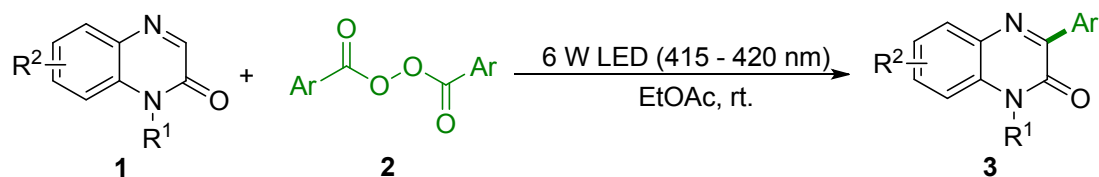
Not use any filters



Figure S2 (Photographed by author Long-Yong Xie)

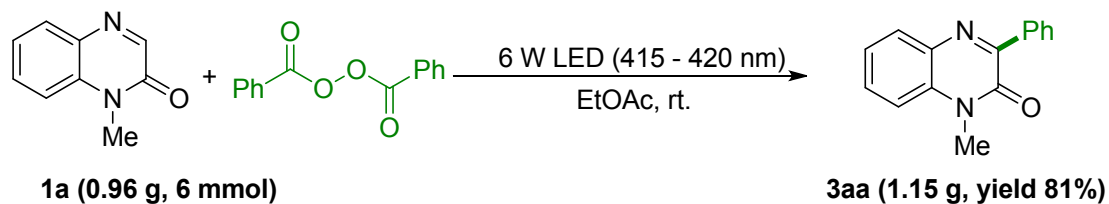
2. Experimental Section

Typical Procedure for the Synthesis of 3-arylquinoxalin-2(1*H*)-ones



To a solution of quinoxalin-2(1*H*)-ones **1** (0.3 mmol) in EtOAc (1.5 mL) was added aryl acyl peroxides **2** (0.45 mmol). The reaction mixture was open to the air and stirred at room temperature under the irradiation of 6 W LED (415 – 420 nm) for about 3h. After completion of the reaction, the resulting mixture was extracted with EtOAc (3 mL × 2) and the organic phase was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent (PE/EA = 6/1-4/1) to give the desired products **3**.

Gram-scale synthesis of **3aa**



To a solution of quinoxalin-2(1*H*)-one **1a** (0.96 g, 6 mmol) in EtOAc (30 mL) was added benzoyl peroxide (2.17 g, 9 mmol). The reaction mixture was open to the air and stirred at

room temperature under the irradiation of 6 W LED (415 – 420 nm) for about 3h. After completion of the reaction, the resulting mixture was extracted with EtOAc (30 mL × 2) and the organic phase was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent (PE/EA = 6/1-4/1) to give 1.15 gram of **3aa**, yield 81%.

Typical Procedure for the Synthesis of Aryl Acyl Peroxides¹

Hydrogen peroxide (1.67 g, 35 wt. % in H₂O, 17 mmol) was added dropwise over 10 min to a cold (ice bath) solution of acid chloride (30 mmol) in diethyl ether (7 mL), followed by dropwise addition of an aqueous solution of NaOH (1.52 g, 38 mmol, 10 mL) over 20 min. The resulting white precipitate was collected by filtration. After washing with water (3 × 5 mL) and diethyl ether (3 × 5 mL), the solid was crystallized from a cold acetone/water mixture (v/v 1: 3).

UV/Vis Absorption Experiment

The UV/Vis absorption spectra of 1-methylquinoxalin-2(1*H*)-one (**1a**, 0.020 M) and 1-methyl-3-phenylquinoxalin-2(1*H*)-one (**3aa**, 0.020 M) in EtOAc were recorded in 1 cm path quartz cuvettes by using a SHIMADZU UV-2600 UV-visible spectrophotometer, respectively. The obtained bands in UV/vis absorption spectra were shown in Figure S3.

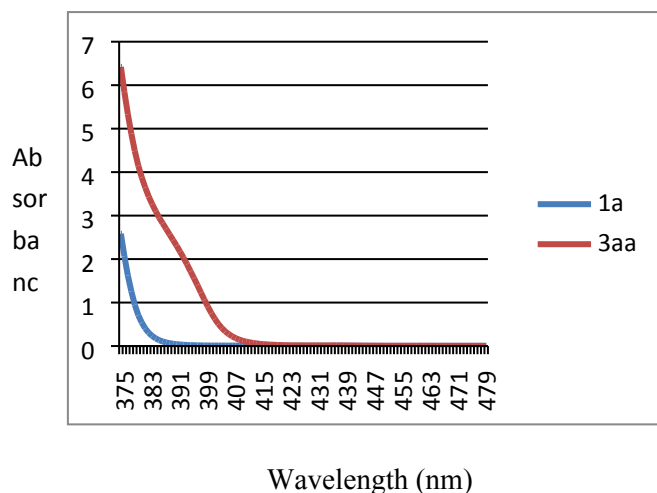


Figure S3 UV-Vis Spectroscopic Measurements on 1a and 3aa

Fluorescence quenching studies

The fluorescence emission intensities were recorded on a Fluormax-4600 spectrofluorimeter. The excitation wavelength was fixed at 288 nm, and the emission wavelength was measured at 419 nm (emission maximum). The samples were prepared by

mixing by quinoxalin-2(*H*)-one **1a** (5.0×10^{-4} mol/L) and different amount of BPO **2a** in EtOAc (total volume = 0.2 mL) in a light path quartz fluorescence cuvette. The concentration of BPO acid stock solution is 1.0×10^{-4} mol/L in EtOAc. For each quenching experiment, 0.1 mL different concentration of BPO acid stock solution was titrated to a mixed solution of 0.1 mL quinoxalin-2(*H*)-one **1a** (in a total volume = 0.2 mL). Then the emission intensity was collected and the results were presented in Figure S4.

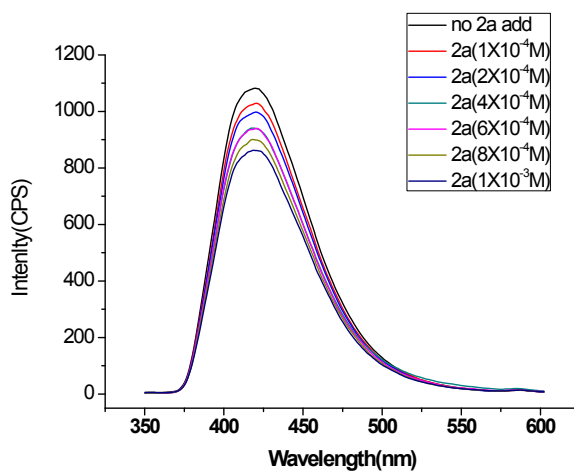
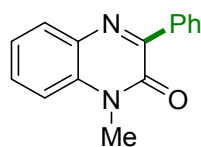


Figure S4 Fluorescence quenching experiment

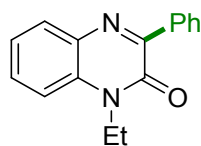
3. Characterization data of products

1-methyl-3-phenylquinoxalin-2(*H*)-one² (**3aa**)



¹H NMR (400 MHz, CDCl₃): δ = 8.32 – 8.30 (m, 2 H), 7.94 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1 H), 7.59 – 7.54 (m, 1 H), 7.49 – 7.47 (m, 3 H), 7.39 – 7.32 (m, 2 H), 3.77 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ = 154.7, 154.1, 136.0, 133.3, 133.1, 130.4, 130.3, 129.5, 128.0, 123.7, 113.5, 29.3.

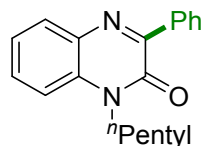
1-ethyl-3-phenylquinoxalin-2(*H*)-one³ (**3ba**)



¹H NMR (400 MHz, CDCl₃): δ = 8.34 – 8.32 (m, 2 H), 7.96 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1 H), 7.57 – 7.53 (m, 1 H), 7.50 – 7.48 (m, 3 H), 7.37 – 7.33 (m, 2 H), 4.38 (q, J = 7.2 Hz, 2 H),

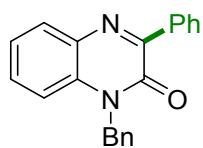
1.42 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.1, 154.0, 136.0, 133.3, 132.2, 130.6, 130.2, 130.2, 129.5, 128.0, 123.4, 113.3, 37.5, 12.3$.

1-pentyl-3-phenylquinoxalin-2(1H)-one (3ca)



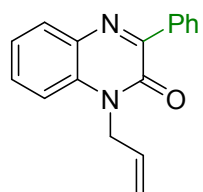
^1H NMR (400 MHz, CDCl_3): $\delta = 8.33 - 8.31$ (m, 2 H), 7.95 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1 H), 7.57 - 7.53 (m, 1 H), 7.50 - 7.47 (m, 3 H), 7.37 - 7.31 (m, 2 H), 4.32 - 4.28 (m, 2 H), 1.82 - 1.79 (m, 2 H), 1.50 - 1.41 (m, 4 H), 0.94 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.3, 154.0, 136.0, 133.3, 132.5, 130.6, 130.2, 130.1, 129.5, 128.0, 123.4, 113.5, 42.5, 29.1, 26.9, 22.4, 13.9$; HRMS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 293.1648, found 293.1646.

1-benzyl-3-phenylquinoxalin-2(1H)-one⁴ (3da)



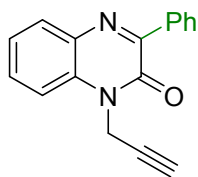
^1H NMR (400 MHz, CDCl_3): $\delta = 8.42 - 8.39$ (m, 2 H), 7.97 (d, $J = 7.6$ Hz, 1 H), 7.52 - 7.51 (m, 3 H), 7.46 - 7.42 (m, 1 H), 7.35 - 7.28 (m, 7 H), 5.57 (s, 2 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.7, 154.1, 135.9, 135.3, 133.3, 132.6, 130.5, 130.3, 130.2, 129.6, 128.8, 128.0, 127.6, 126.9, 123.7, 114.3, 46.0$.

1-allyl-3-phenylquinoxalin-2(1H)-one⁵ (3ea)



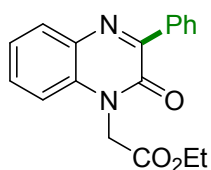
^1H NMR (400 MHz, CDCl_3): $\delta = 8.34 - 8.32$ (m, 2 H), 7.96 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.0$ Hz, 1 H), 7.56 - 7.47 (m, 4 H), 7.38 - 7.31 (m, 2 H), 6.02 - 5.96 (m, 1 H), 5.31 - 5.21 (m, 2 H), 4.99 - 4.97 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.2, 154.1, 135.9, 133.3, 132.6, 130.6, 130.5, 130.3, 130.2, 129.6, 128.0, 123.7, 118.1, 114.1, 44.7$.

3-phenyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one³ (3fa)



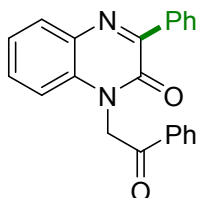
^1H NMR (400 MHz, CDCl_3): δ = 8.34 – 8.31 (m, 2 H), 7.96 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.61 – 7.57 (m, 1 H), 7.50 – 7.47 (m, 4 H), 7.41 – 7.37 (m, 1 H), 5.11 (d, J = 2.4 Hz, 2 H), 2.32 – 2.31 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 153.9, 153.6, 135.7, 133.2, 131.8, 130.5, 130.4, 130.4, 129.5, 128.0, 124.1, 114.0, 73.1, 31.6.

ethyl 2-(2-oxo-3-phenylquinoxalin-1(2H)-yl)acetate⁴ (3ga)



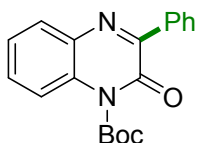
^1H NMR (400 MHz, CDCl_3): δ = 8.34 – 8.31 (m, 2 H), 7.97 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.55 – 7.47 (m, 4 H), 7.39 – 7.35 (m, 1 H), 7.11 – 7.09 (m, 1 H), 5.08 (s, 2 H), 4.26 (q, J = 7.2 Hz, 2 H), 1.29 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 167.1, 154.2, 153.8, 135.6, 133.1, 132.4, 130.7, 130.4, 129.5, 128.0, 124.0, 113.0, 62.0, 43.7, 14.1.

1-(2-oxo-2-phenylethyl)-3-phenylquinoxalin-2(1H)-one³ (3ha)



^1H NMR (400 MHz, CDCl_3): δ = 8.26 – 8.24 (m, 2 H), 8.06 – 8.04 (m, 2 H), 7.93 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1 H), 7.64 – 7.61 (m, 1 H), 7.52 – 7.49 (m, 2 H), 7.43 – 7.39 (m, 4 H), 7.32 – 7.28 (m, 1 H), 6.94 – 6.92 (m, 1 H), 5.75 (s, 2 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 191.2, 154.4, 153.8, 135.8, 134.5, 134.3, 133.3, 132.8, 130.7, 130.4, 129.6, 129.0, 128.2, 128.1, 123.9, 113.4, 48.6.

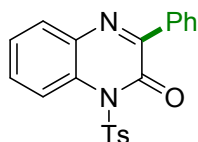
tert-butyl 2-(2-oxo-3-phenylquinoxaline-1(2H)-yl)carboxylate (3ia)



^1H NMR (400 MHz, CDCl_3): δ = 8.33 – 8.31 (m, 2 H), 7.95 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1

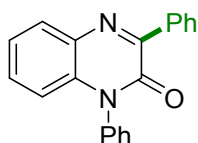
H), 7.55 – 7.47 (m, 4 H), 7.41 – 7.37 (m, 1 H), 7.13 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, 1 H), 1.72 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.4, 152.3, 149.5, 132.3, 130.7, 130.5, 130.3, 129.6, 129.4, 128.2, 124.6, 113.2, 87.8, 27.6$; HRMS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 323.1390, found 323.1394.

3-phenyl-1-tosylquinoxalin-2(1H)-one (3ja)



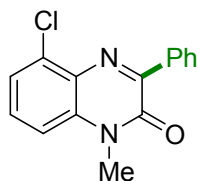
^1H NMR (400 MHz, CDCl_3): $\delta = 8.14 - 8.12$ (m, 1 H), 7.99 – 7.92 (m, 5 H), 7.76 – 7.74 (m, 2 H), 7.51 – 7.49 (m, 3 H), 7.32 (d, $J = 8.0$ Hz, 2 H), 2.45 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 149.3, 146.9, 145.6, 141.2, 138.9, 134.6, 133.9, 130.5, 130.1, 129.8, 129.6, 129.5, 129.1, 129.1, 128.5, 127.9, 21.7$; HRMS (ESI) m/z calcd. for $\text{C}_{21}\text{H}_{17}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 377.0954, found 377.0951.

1,3-diphenylquinoxalin-2(1H)-one⁴ (3ka)



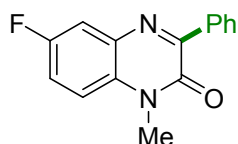
^1H NMR (400 MHz, CDCl_3): $\delta = 8.42 - 8.39$ (m, 2 H), 8.01 – 7.99 (m, 1 H), 7.66 – 7.63 (m, 2 H), 7.59 – 7.56 (m, 1 H), 7.50 – 7.46 (m, 3 H), 7.37 – 7.34 (m, 4 H), 6.71 – 6.69 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.5, 154.5, 136.1, 135.7, 134.1, 133.0, 130.5, 130.3, 130.0, 129.9, 129.7, 129.4, 128.3, 128.0, 123.9, 115.3$.

5-chloro-1-methyl-3-phenylquinoxalin-2(1H)-one (3la)



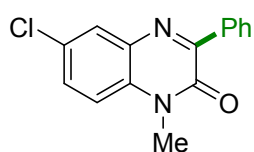
^1H NMR (400 MHz, CDCl_3): $\delta = 8.47 - 8.44$ (m, 2 H), 8.11 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1 H), 7.50 – 7.48 (m, 2 H), 7.42 – 7.40 (m, 2 H), 7.20 – 7.18 (m, 1 H), 3.73 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.2, 153.5, 135.1, 134.6, 133.6, 130.7, 130.1, 129.8, 128.4, 128.1, 124.5, 112.4, 29.7$; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{12}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 271.0633, found 271.0632.

6-fluoro-1-methyl-3-phenylquinoxalin-2(1H)-one⁴ (3ma)



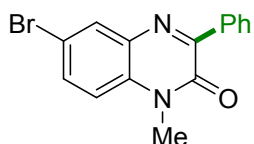
^1H NMR (400 MHz, CDCl_3): δ = 8.33 – 8.31 (m, 2 H), 7.63 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1 H), 7.50 – 7.47 (m, 3 H), 7.32 – 7.27 (m, 2 H), 3.76 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 158.7 (d, $J_{\text{C-F}}$ = 244.3), 155.3, 154.3, 135.7, 133.6 (d, $J_{\text{C-F}}$ = 11.7 Hz), 130.6, 130.0, 129.6, 128.1, 118.0 (d, $J_{\text{C-F}}$ = 24.0 Hz), 115.6 (d, $J_{\text{C-F}}$ = 22.6 Hz), 114.6 (d, $J_{\text{C-F}}$ = 8.8 Hz), 29.5; ^{19}F NMR (376 MHz, CDCl_3): δ = -118.9.

6-chloro-1-methyl-3-phenylquinoxalin-2(1H)-one⁶ (3na)



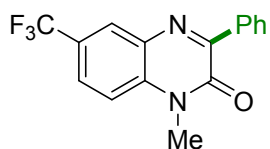
^1H NMR (400 MHz, CDCl_3): δ = 8.31 – 8.29 (m, 2 H), 7.93 (d, J = 2.8 Hz, 1 H), 7.53 – 7.47 (m, 4 H), 7.26 (d, J = 9.2 Hz, 1 H), 3.75 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 155.2, 154.3, 135.6, 133.6, 132.0, 130.7, 130.2, 129.6, 129.6, 129.0, 128.1, 114.7, 29.5.

6-bromo-1-methyl-3-phenylquinoxalin-2(1H)-one⁴ (3oa)



^1H NMR (400 MHz, CDCl_3): δ = 8.31 – 8.29 (m, 2 H), 8.08 (d, J = 2.8 Hz, 1 H), 7.63 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1 H), 7.50 – 7.46 (m, 3 H), 7.19 (d, J = 9.2 Hz, 1 H), 3.73 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 155.1, 154.3, 135.6, 133.8, 132.9, 132.6, 132.4, 130.7, 129.6, 128.1, 116.2, 115.0, 29.4.

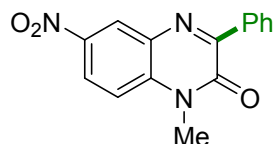
1-methyl-3-phenyl-6-(trifluoromethyl)quinoxalin-2(1H)-one (3pa)



^1H NMR (400 MHz, CDCl_3): δ = 8.34 – 8.31 (m, 2 H), 8.20 (d, J = 1.6 Hz, 1 H), 7.75 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1 H), 7.51 – 7.44 (m, 3 H), 7.39 (d, J = 8.8 Hz, 1 H), 3.75 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 155.3, 154.4, 135.3, 133.6, 130.8, 130.1, 129.6, 128.1, 127.7 (q, $J_{\text{C-F}}$ = 3.7 Hz), 126.4 (q, $J_{\text{C-F}}$ = 3.6 Hz), 125.9 (q, $J_{\text{C-F}}$ = 33.5 Hz), 123.7 (q, $J_{\text{C-F}}$ = 269.8 Hz),

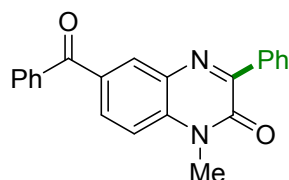
114.2, 29.5; ^{19}F NMR (376 MHz, CDCl_3): $\delta = -62.0$; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{12}\text{F}_3\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 305.0896, found 305.0891.

1-methyl-6-nitro-3-phenylquinoxalin-2(1H)-one³ (3qa)



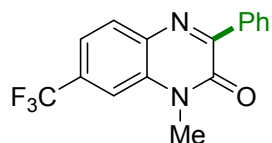
^1H NMR (400 MHz, CDCl_3): $\delta = 8.81$ (d, $J = 2.4$ Hz, 1 H), 8.41 (dd, $J_1 = 9.2$ Hz, $J_2 = 2.4$ Hz, 1 H), 8.35 – 8.32 (m, 2 H), 7.54 – 7.48 (m, 3 H), 7.43 (d, $J = 9.2$ Hz, 1 H), 3.81 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 156.1, 154.2, 143.4, 137.8, 134.9, 132.1, 131.3, 129.7, 128.2, 126.0, 124.6, 114.2, 29.9$.

6-benzoyl-1-methyl-3-phenylquinoxalin-2(1H)-one (3ra)



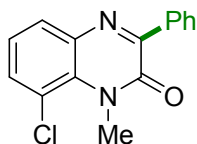
^1H NMR (400 MHz, CDCl_3): $\delta = 8.37 - 8.34$ (m, 2 H), 8.00 (d, $J = 8.0$ Hz, 1 H), 7.85 – 7.82 (m, 3 H), 7.72 – 7.69 (m, 1 H), 7.66 – 7.62 (m, 1 H), 7.55 – 7.49 (m, 5 H), 3.78 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 195.5, 156.1, 154.5, 138.4, 137.0, 135.6, 135.2, 133.3, 132.9, 130.9, 130.0, 129.7, 128.5, 128.1, 125.2, 115.3, 29.5$; HRMS (ESI) m/z calcd. for $\text{C}_{22}\text{H}_{17}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 341.1285, found 341.1288.

1-methyl-3-phenyl-7-(trifluoromethyl)quinoxalin-2(1H)-one (3sa)



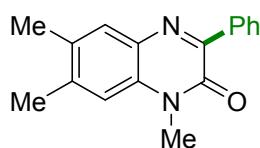
^1H NMR (400 MHz, CDCl_3): $\delta = 8.34 - 8.31$ (m, 2 H), 8.01 (d, $J = 8.4$ Hz, 1 H), 7.59 – 7.54 (m, 2 H), 7.51 – 7.45 (m, 3 H), 3.76 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 156.1, 154.3, 135.3, 134.6, 133.2, 131.5$ (q, $J_{\text{C-F}} = 33.3$ Hz), 131.0, 129.7, 128.1, 123.6 (q, $J_{\text{C-F}} = 3.7$ Hz), 120.1 (q, $J_{\text{C-F}} = 270.5$ Hz), 111.0 (q, $J_{\text{C-F}} = 3.7$ Hz), 29.4; ^{19}F NMR (376 MHz, CDCl_3): $\delta = -62.3$; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{12}\text{F}_3\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 305.0896, found 305.0893.

8-chloro-1-methyl-3-phenylquinoxalin-2(1H)-one (3ta)



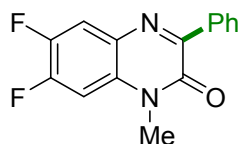
^1H NMR (400 MHz, CDCl_3): $\delta = 8.33 - 8.30$ (m, 2 H), 7.86 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1 H), 7.58 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1 H), 7.52 – 7.49 (m, 3 H), 7.30 – 7.28 (m, 1 H), 4.10 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 155.8, 154.1, 135.4, 135.3, 133.3, 131.6, 130.7, 129.9, 129.6, 128.1, 124.1, 119.5, 35.9$; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{12}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 271.0633, found 271.0631.

1,6,7-trimethyl-3-phenylquinoxalin-2(1H)-one⁷ (3ua)



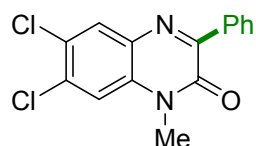
^1H NMR (400 MHz, CDCl_3): $\delta = 8.30 - 8.27$ (m, 2 H), 7.70 (s, 1 H), 7.48 – 7.46 (m, 3 H), 7.09 (s, 1 H), 3.74 (s, 3 H), 2.43 (s, 3 H), 2.37 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.8, 152.9, 140.3, 136.3, 132.7, 131.6, 131.4, 130.4, 129.9, 129.4, 128.0, 114.1, 29.2, 20.6, 19.2$.

6,7-difluoro-1-methyl-3-phenylquinoxalin-2(1H)-one (3va)



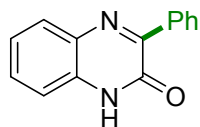
^1H NMR (400 MHz, CDCl_3): $\delta = 8.29 - 8.27$ (m, 2 H), 7.76 – 7.71 (m, 1 H), 7.50 – 7.45 (m, 3 H), 7.14 – 7.10 (m, 1 H), 3.71 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.3$ (d, $J = 3.7$ Hz), 154.2, 151.5 (dd, $J_1 = 252.3$ Hz, $J_2 = 13.7$ Hz), 146.8 (dd, $J_1 = 245.7$ Hz, $J_2 = 13.9$ Hz), 135.5, 130.7, 130.5 (dd, $J_1 = 9.5$ Hz, $J_2 = 2.2$ Hz), 129.5, 129.3 (dd, $J_1 = 9.5$ Hz, $J_2 = 2.5$ Hz), 128.1, 117.8 (dd, $J_1 = 18.2$ Hz, $J_2 = 2.2$ Hz), 102.2 (d, $J_{\text{C-F}} = 22.6$ Hz), 29.8; ^{19}F NMR (376 MHz, CDCl_3): $\delta = -130.5$ (d, $J_{\text{F-F}} = 23.3$ Hz, 1 F), -141.9 (d, $J_{\text{F-F}} = 21.8$ Hz, 1 F); HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{11}\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 273.0834, found 273.0828.

6,7-dichloro-1-methyl-3-phenylquinoxalin-2(1H)-one² (3wa)



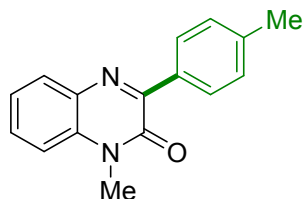
^1H NMR (400 MHz, CDCl_3): $\delta = 8.30 - 8.28$ (m, 2 H), 7.99 (s, 1 H), 7.51 – 7.47 (m, 3 H), 7.40 (s, 1 H), 3.69 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 155.0, 154.1, 135.3, 134.2, 132.6, 132.1, 131.0, 130.9, 129.6, 128.1, 127.5, 115.0, 29.5$.

3-phenylquinoxalin-2(1H)-one⁸ (3xa)



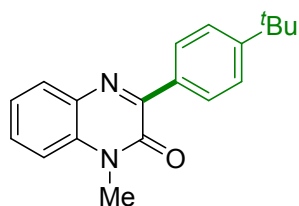
^1H NMR (400 MHz, d^6 -DMSO): $\delta = 8.28 - 8.25$ (m, 2 H), 7.82 (dd, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1 H), 7.55 – 7.45 (m, 4 H), 7.34 – 7.30 (m, 2 H); ^{13}C NMR (100 MHz, d^6 -DMSO): $\delta = 155.3, 154.9, 136.3, 132.7, 132.7, 131.1, 130.9, 129.9, 129.5, 128.6, 124.2, 115.8$.

1-methyl-3-(p-tolyl)quinoxalin-2(1H)-one⁹ (3ab)



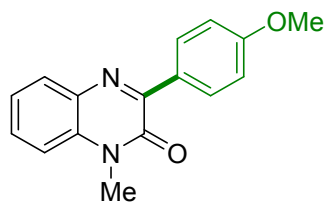
^1H NMR (400 MHz, CDCl_3): $\delta = 8.25$ (d, $J = 8.0$ Hz, 2 H), 7.92 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1 H), 7.56 – 7.51 (m, 1 H), 7.37 – 7.28 (m, 4 H), 3.75 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.7, 153.9, 140.6, 133.3, 133.2, 133.1, 130.3, 130.0, 129.5, 128.8, 123.6, 113.5, 29.2, 21.5$.

3-(4-(tert-butyl)phenyl)-1-methylquinoxalin-2(1H)-one¹⁰ (3ac)



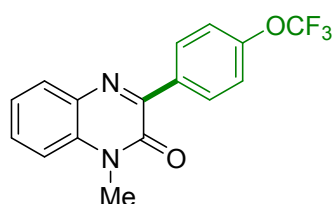
^1H NMR (400 MHz, CDCl_3): $\delta = 8.26 - 8.24$ (m, 2 H), 7.93 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1 H), 7.57 – 7.50 (m, 3 H), 7.38 – 7.31 (m, 2 H), 3.76 (s, 3 H), 1.37 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.7, 154.1, 153.6, 133.2, 133.2, 130.3, 130.0, 129.2, 125.1, 123.6, 113.5, 34.8, 31.2, 29.2$.

3-(4-methoxyphenyl)-1-methylquinoxalin-2(1H)-one⁹ (3ad)



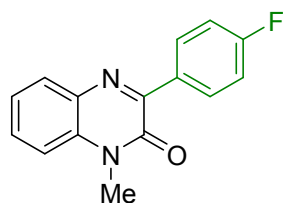
^1H NMR (400 MHz, CDCl_3): δ = 8.41 – 8.37 (m, 2 H), 7.90 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.54 – 7.50 (m, 1 H), 7.36 – 7.29 (m, 2 H), 7.01 – 6.97 (m, 2 H), 3.87 (s, 3 H), 3.75 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 161.4, 153.1, 133.1, 133.1, 131.3, 130.1, 129.7, 128.7, 123.6, 113.5, 113.4, 55.3, 29.2.

1-methyl-3-(4-(trifluoromethoxy)phenyl)quinoxalin-2(1H)-one¹⁰ (3ae)



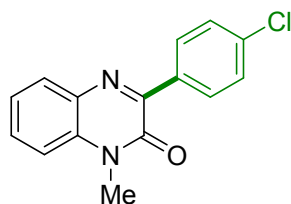
^1H NMR (400 MHz, CDCl_3): δ = 8.44 – 8.40 (m, 2 H), 7.94 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.62 – 7.58 (m, 1 H), 7.41 – 7.33 (m, 4 H), 3.78 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 154.6, 152.5, 150.7 (q, J = 2.2 Hz), 134.5, 133.4, 133.0, 131.3, 130.7, 130.5, 123.9, 120.4 (q, J = 256.0 Hz), 120.2, 113.6, 29.3; ^{19}F NMR (376 MHz, CDCl_3): δ = -57.6.

3-(4-fluorophenyl)-1-methylquinoxalin-2(1H)-one⁹ (3af)



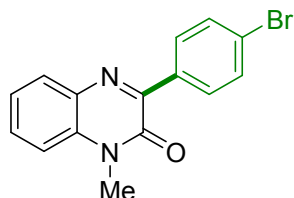
^1H NMR (400 MHz, CDCl_3): δ = 8.40 – 8.36 (m, 2 H), 7.91 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.58 – 7.54 (m, 1 H), 7.38 – 7.31 (m, 2 H), 7.17 – 7.13 (m, 2 H), 3.75 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 164.1 (d, $J_{\text{C-F}}$ = 249.3 Hz), 154.6, 152.7, 133.2, 132.9, 132.1 (d, $J_{\text{C-F}}$ = 2.9 Hz), 131.8, 131.7, 130.3 (d, $J_{\text{C-F}}$ = 1.5 Hz), 123.8, 115.0 (d, $J_{\text{C-F}}$ = 21.1 Hz), 113.6, 29.3; ^{19}F NMR (376 MHz, CDCl_3): δ = -110.0.

3-(4-chlorophenyl)-1-methylquinoxalin-2(1H)-one⁴ (3ag)



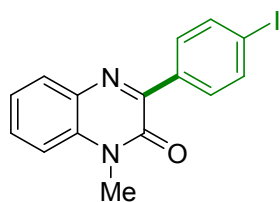
^1H NMR (400 MHz, CDCl_3): δ = 8.36 – 8.32 (m, 2 H), 7.93 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.60 – 7.56 (m, 1 H), 7.45 – 7.43 (m, 2 H), 7.39 – 7.32 (m, 2 H), 3.76 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 154.6, 152.6, 136.5, 134.4, 133.3, 132.9, 131.0, 130.5, 130.4, 128.2, 123.8, 113.6, 29.3.

3-(4-bromophenyl)-1-methylquinoxalin-2(1H)-one⁶ (3ah)



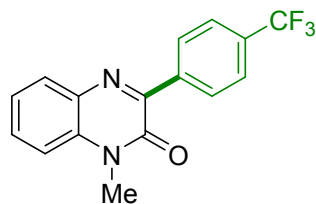
^1H NMR (400 MHz, CDCl_3): δ = 8.29 – 8.25 (m, 2 H), 7.93 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.61 – 7.56 (m, 3 H), 7.40 – 7.33 (m, 2 H), 3.77 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 154.5, 152.7, 134.9, 133.3, 133.0, 131.2, 130.6, 130.5, 125.1, 123.9, 113.6, 29.3.

3-(4-iodophenyl)-1-methylquinoxalin-2(1H)-one⁹ (3ai)



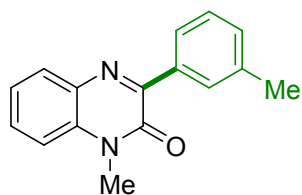
^1H NMR (400 MHz, CDCl_3): δ = 8.14 – 8.10 (m, 2 H), 7.94 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.84 – 7.81 (m, 2 H), 7.61 – 7.57 (m, 1 H), 7.40 – 7.33 (m, 2 H), 3.77 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 154.6, 137.3, 135.5, 133.4, 133.0, 131.2, 130.6, 130.5, 129.5, 123.9, 113.6, 97.4, 29.3.

1-methyl-3-(4-(trifluoromethyl)phenyl)quinoxalin-2(1H)-one¹¹ (3aj)



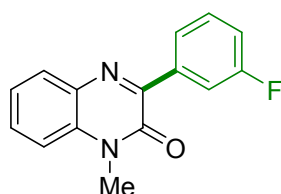
^1H NMR (400 MHz, CDCl_3): δ = 8.46 (d, J = 8.0 Hz, 2 H), 7.97 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.75 – 7.72 (m, 2 H), 7.64 – 7.60 (m, 1 H), 7.43 – 7.36 (m, 2 H), 3.79 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 154.6, 152.6, 139.3, 133.5, 133.0, 131.8 (q, $J_{\text{C-F}}$ = 32.8 Hz), 131.0, 130.7, 129.9, 124.9 (q, $J_{\text{C-F}}$ = 3.7 Hz), 124.1 (q, $J_{\text{C-F}}$ = 270.5 Hz), 124.0, 113.7, 29.4.

1-methyl-3-(m-tolyl)quinoxalin-2(1H)-one⁷ (3ak)



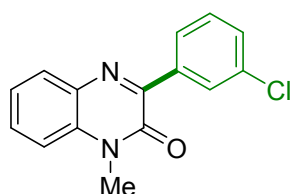
^1H NMR (400 MHz, CDCl_3): δ = 8.10 – 8.08 (m, 2 H), 7.95 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.58 – 7.54 (m, 1 H), 7.39 – 7.29 (m, 4 H), 3.76 (s, 3 H), 2.45 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 154.7, 154.4, 137.6, 136.0, 133.3, 133.1, 131.1, 130.4, 130.2, 129.9, 127.9, 126.7, 123.7, 113.5, 29.2, 21.5.

3-(3-fluorophenyl)-1-methylquinoxalin-2(1H)-one³ (3a)



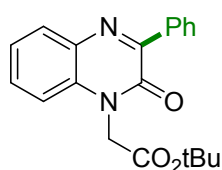
^1H NMR (400 MHz, CDCl_3): δ = 8.19 – 8.17 (m, 1 H), 8.13 – 8.09 (m, 1 H), 7.93 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.60 – 7.56 (m, 1 H), 7.46 – 7.32 (m, 3 H), 7.20 – 7.15 (m, 1 H), 3.76 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 162.5 (d, $J_{\text{C-F}}$ = 242.8 Hz), 154.5, 152.3, 138.0 (d, $J_{\text{C-F}}$ = 8.0 Hz), 133.3, 132.8, 130.7, 130.5, 129.4 (d, $J_{\text{C-F}}$ = 8.0 Hz), 125.3 (d, $J_{\text{C-F}}$ = 3.0 Hz), 123.8, 117.2 (d, $J_{\text{C-F}}$ = 21.2 Hz), 116.5 (d, $J_{\text{C-F}}$ = 23.3 Hz), 113.6, 29.3.

3-(3-chlorophenyl)-1-methylquinoxalin-2(1H)-one⁹ (3am)



^1H NMR (400 MHz, CDCl_3): δ = 8.36 – 8.35 (m, 1 H), 8.29 – 8.26 (m, 1 H), 7.93 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.60 – 7.56 (m, 1 H), 7.45 – 7.31 (m, 4 H), 3.75 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 154.4, 152.3, 137.6, 134.0, 133.3, 132.8, 130.7, 130.5, 130.2, 129.5, 129.2, 127.7, 123.8, 113.6, 29.3.

tert-butyl 2-(2-oxo-3-phenylquinoxalin-1(2H)-yl)acetate⁶ (3ua)



¹H NMR (400 MHz, CDCl₃): δ = 8.34 – 8.31 (m, 2 H), 7.96 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.6 Hz, 1 H), 7.54 – 7.48 (m, 4 H), 7.37 – 7.34 (m, 1 H), 7.10 – 7.08 (m, 1 H), 5.00 (s, 2 H), 1.48 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ = 166.1, 154.2, 153.8, 135.7, 133.1, 132.5, 130.6, 130.3, 130.3, 129.5, 128.0, 123.8, 113.0, 83.1, 44.3, 27.9.

4. References

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5. ^1H and ^{13}C NMR spectra of products

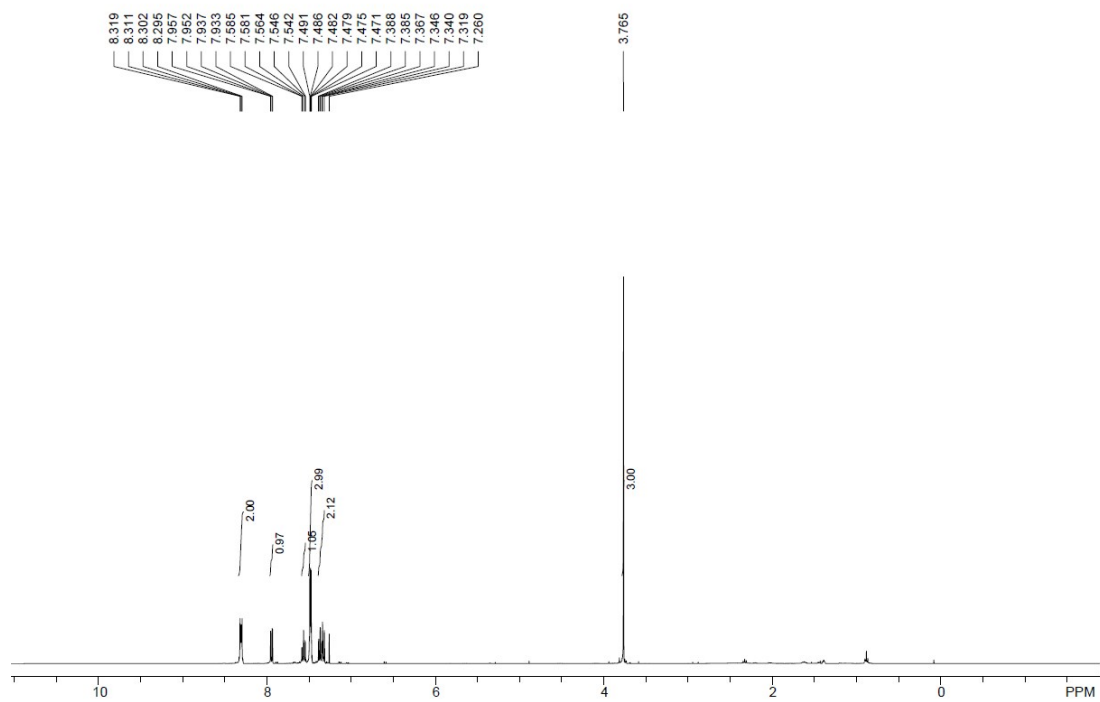


Figure S1. ^1H spectra of **3aa**

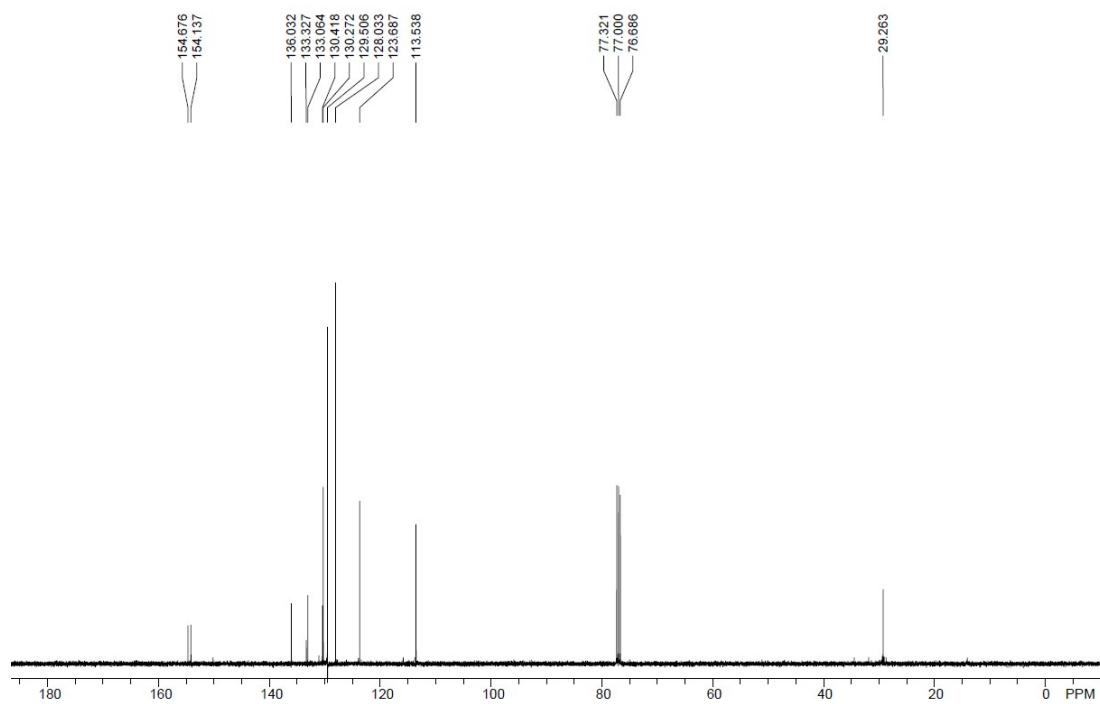


Figure S2. ^{13}C spectra of **3aa**

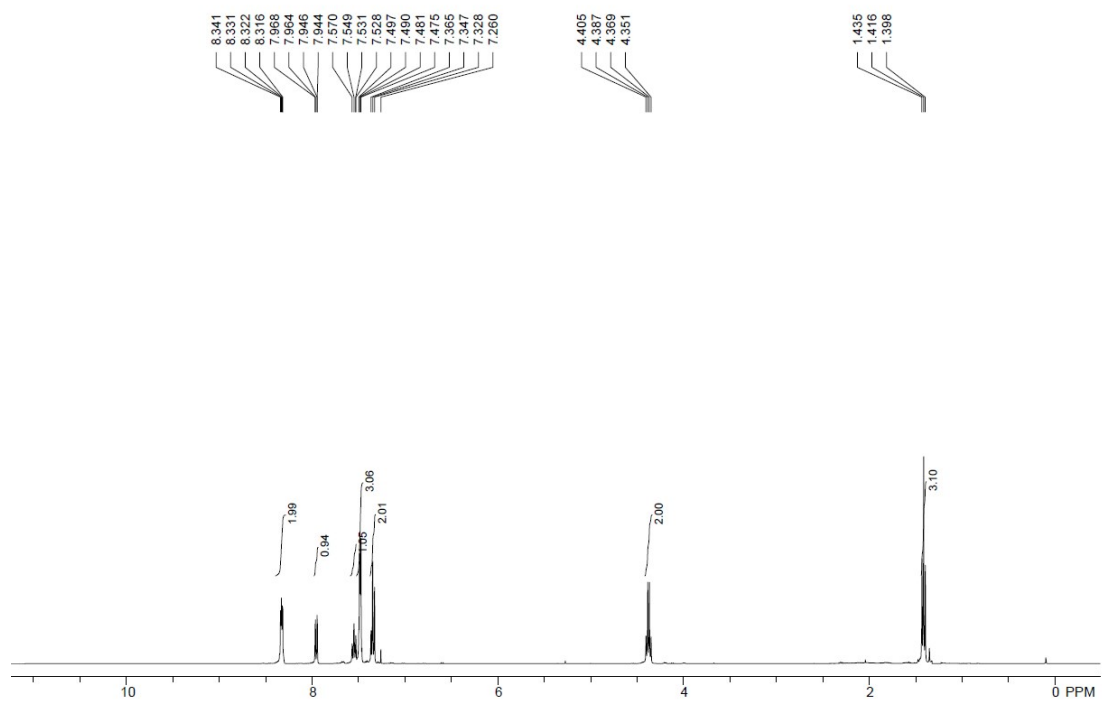


Figure S3. ^1H spectra of **3ba**

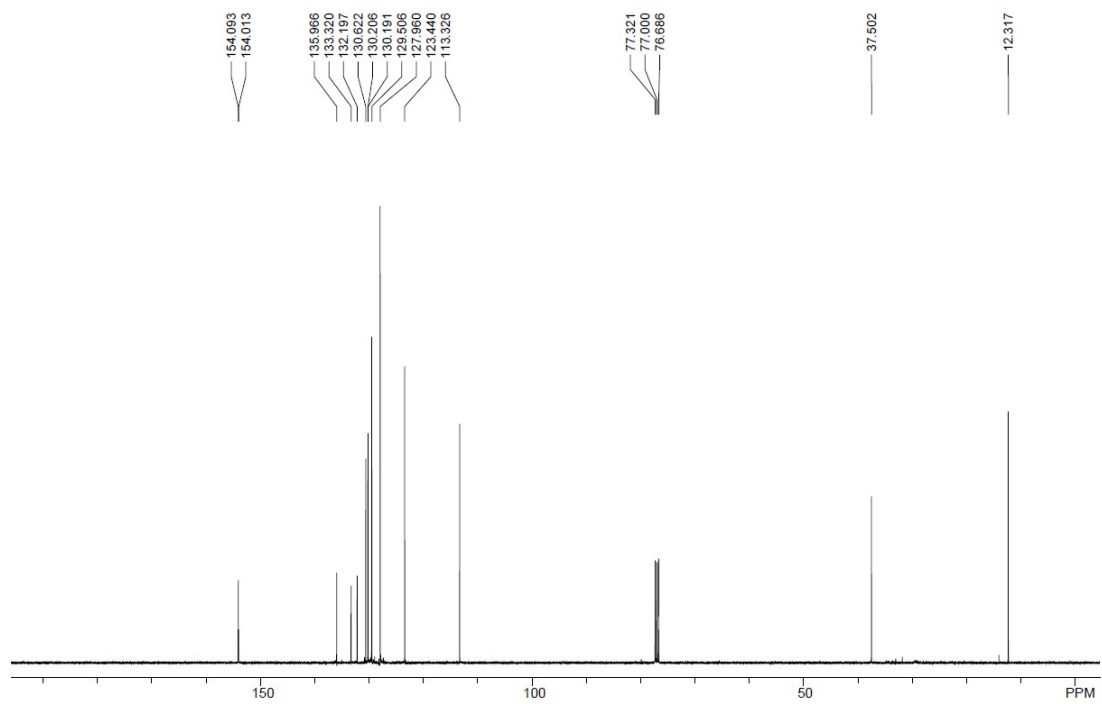


Figure S4. ^{13}C spectra of **3ba**

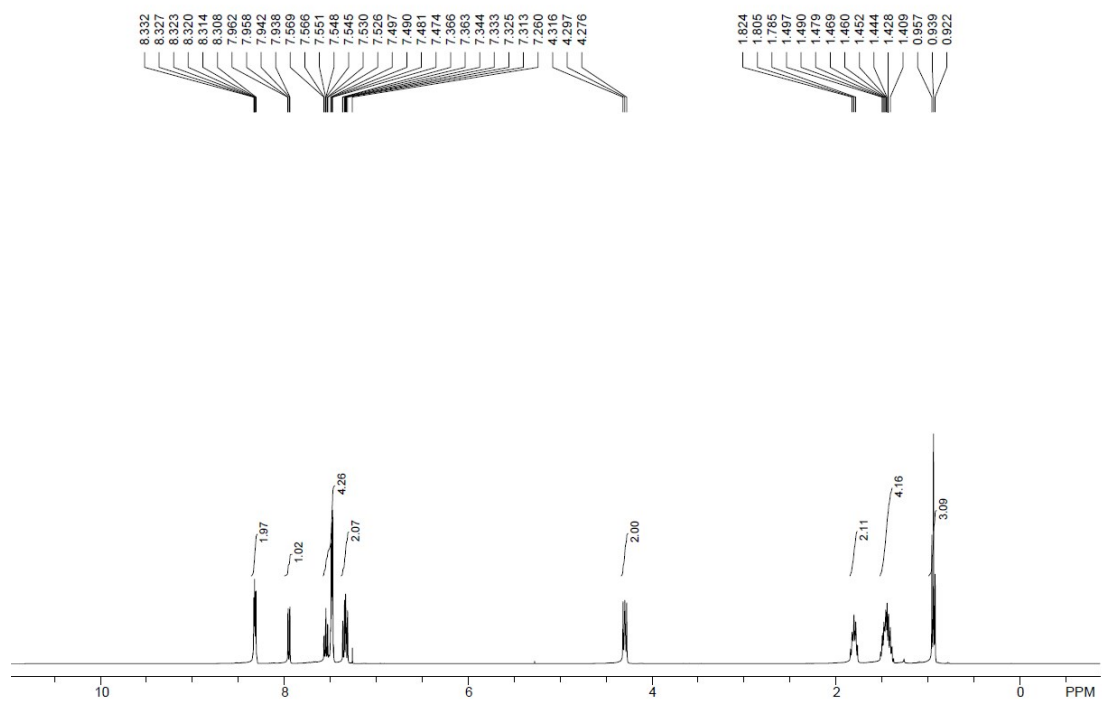


Figure S5. ^1H spectra of **3ca**

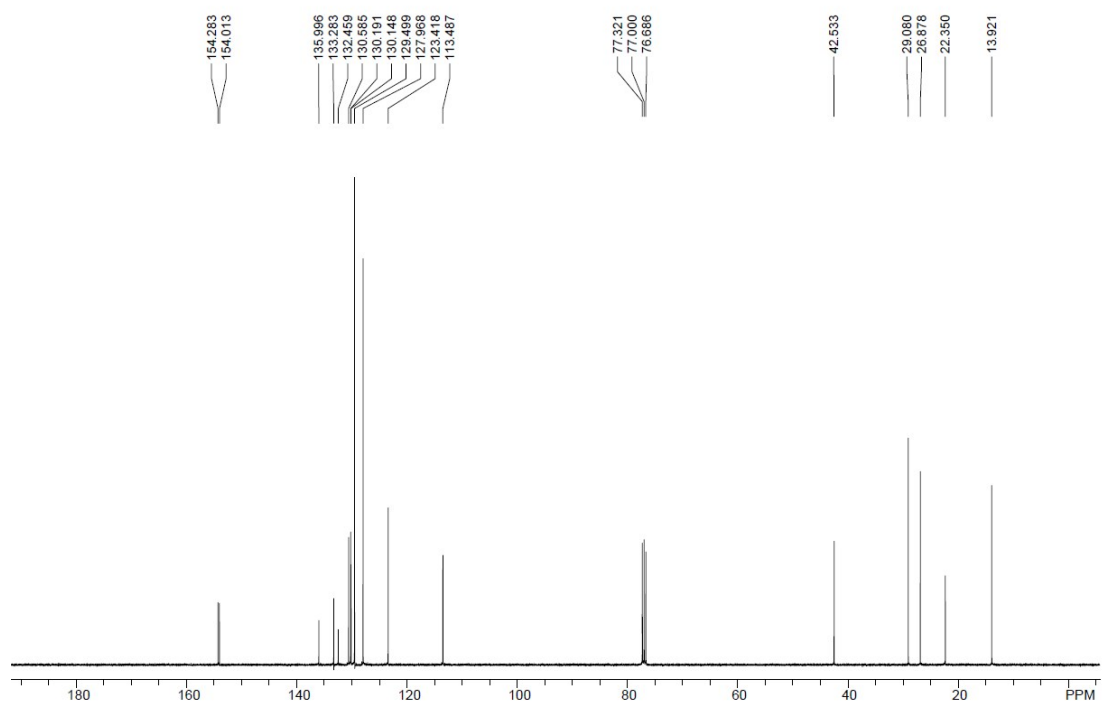


Figure S6. ^{13}C spectra of **3ca**

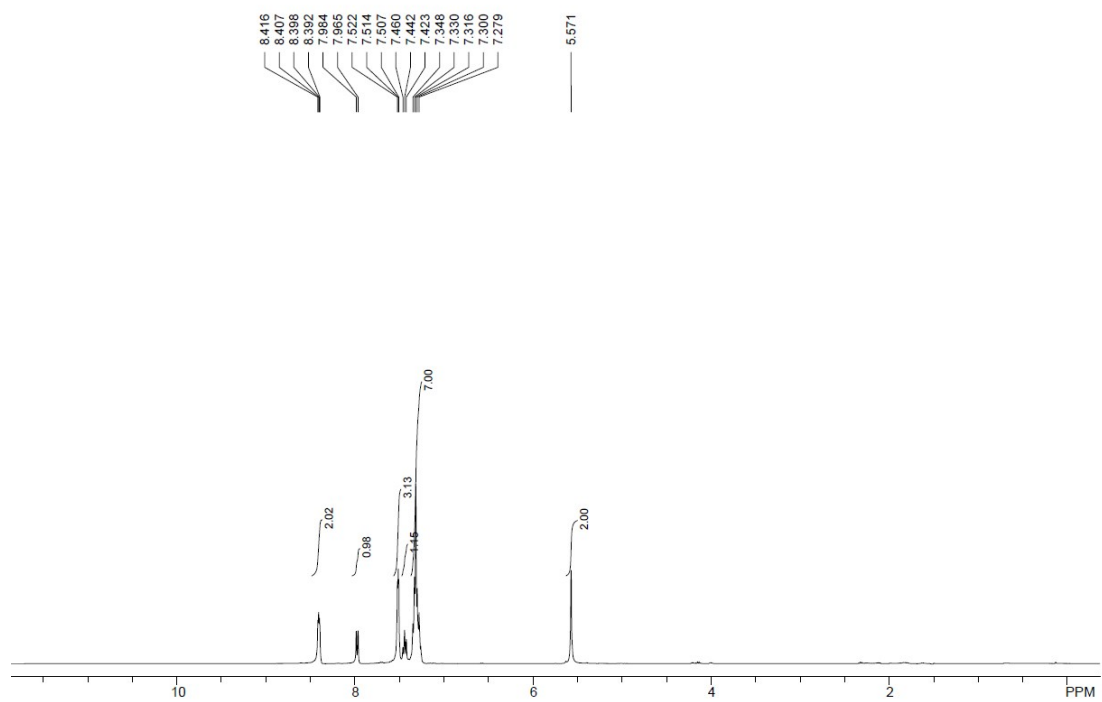


Figure S7. ^1H spectra of **3da**

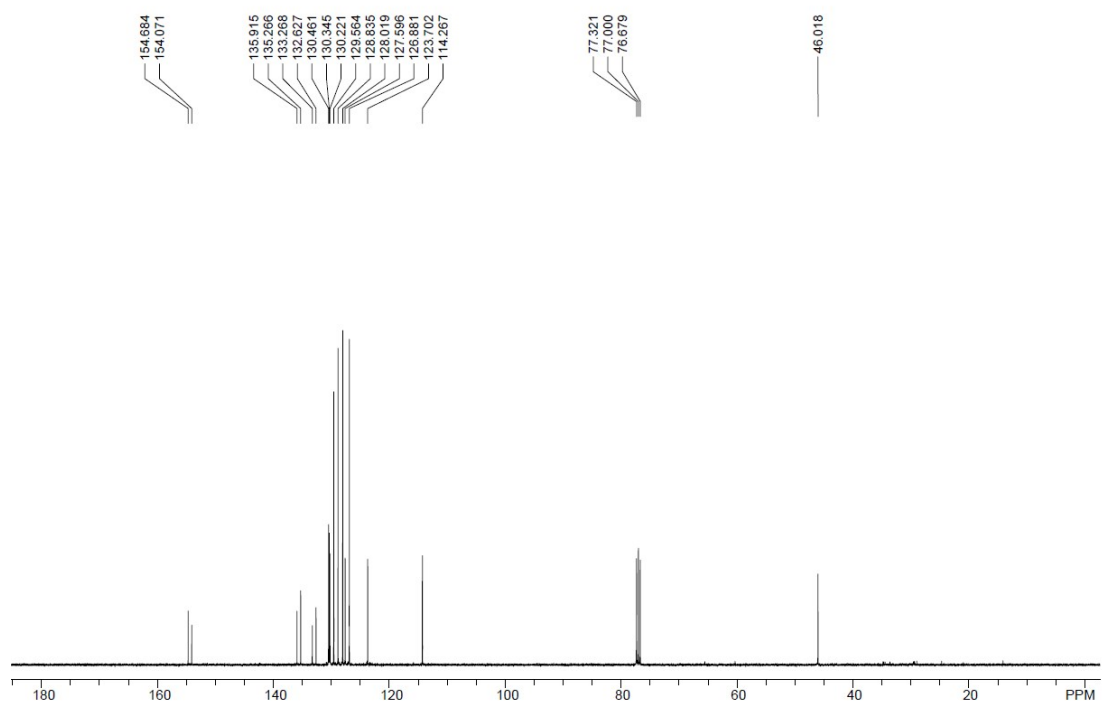


Figure S8. ^{13}C spectra of **3da**

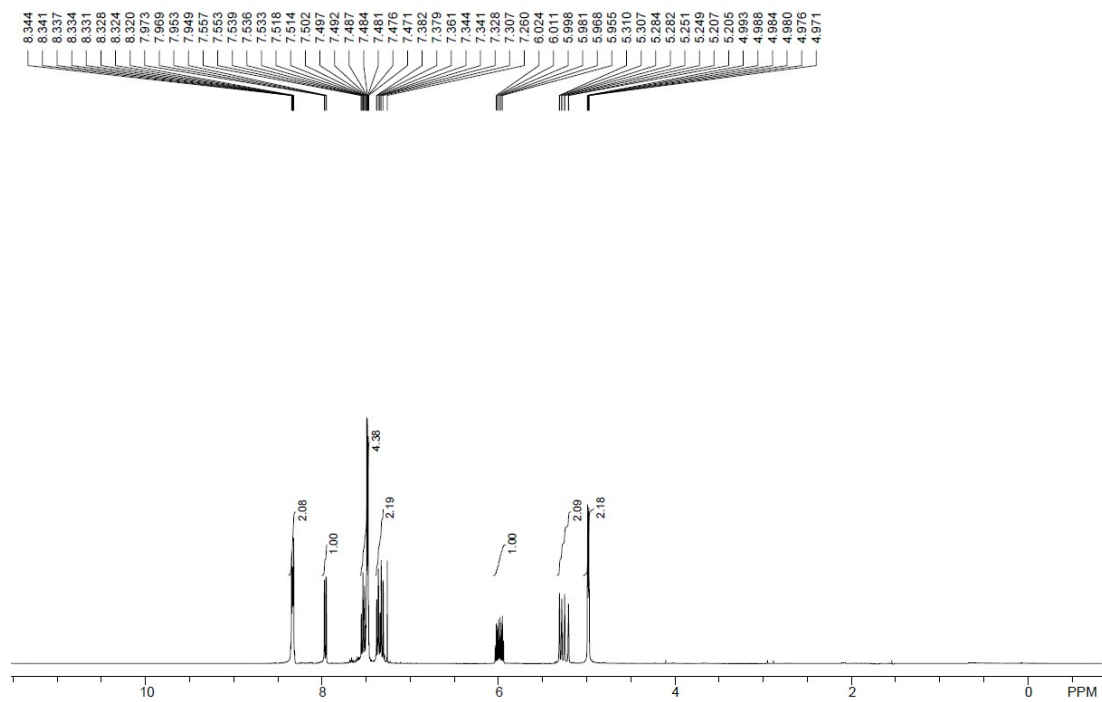


Figure S9. ^1H spectra of **3ea**

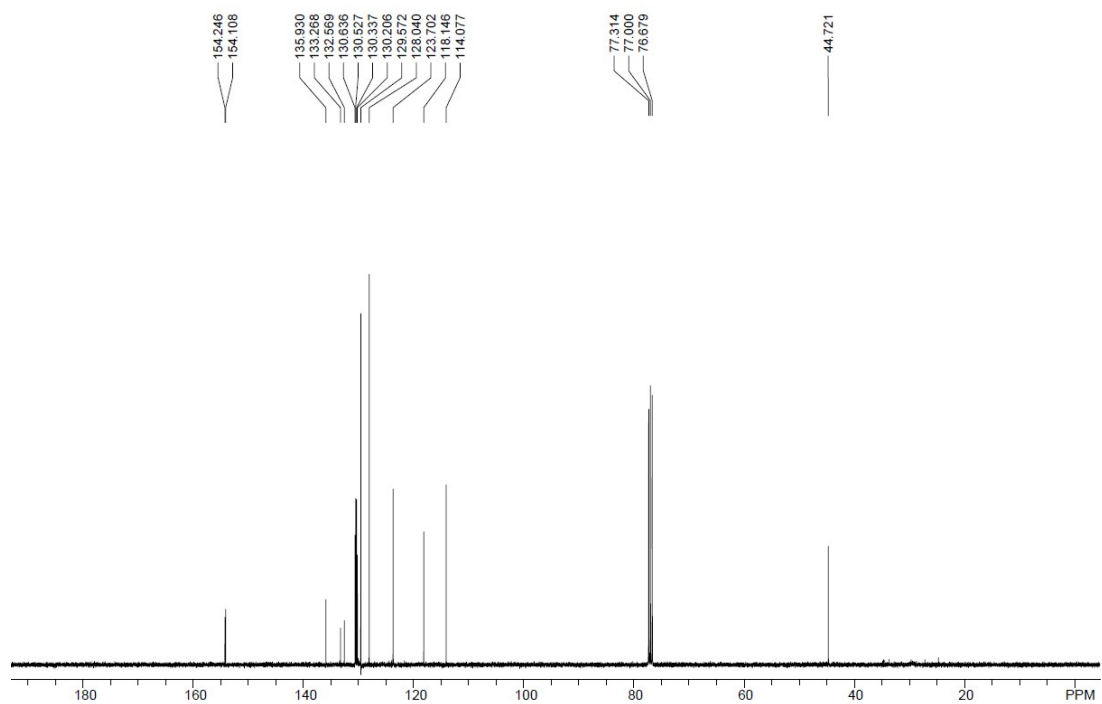


Figure S10. ^{13}C spectra of **3ea**

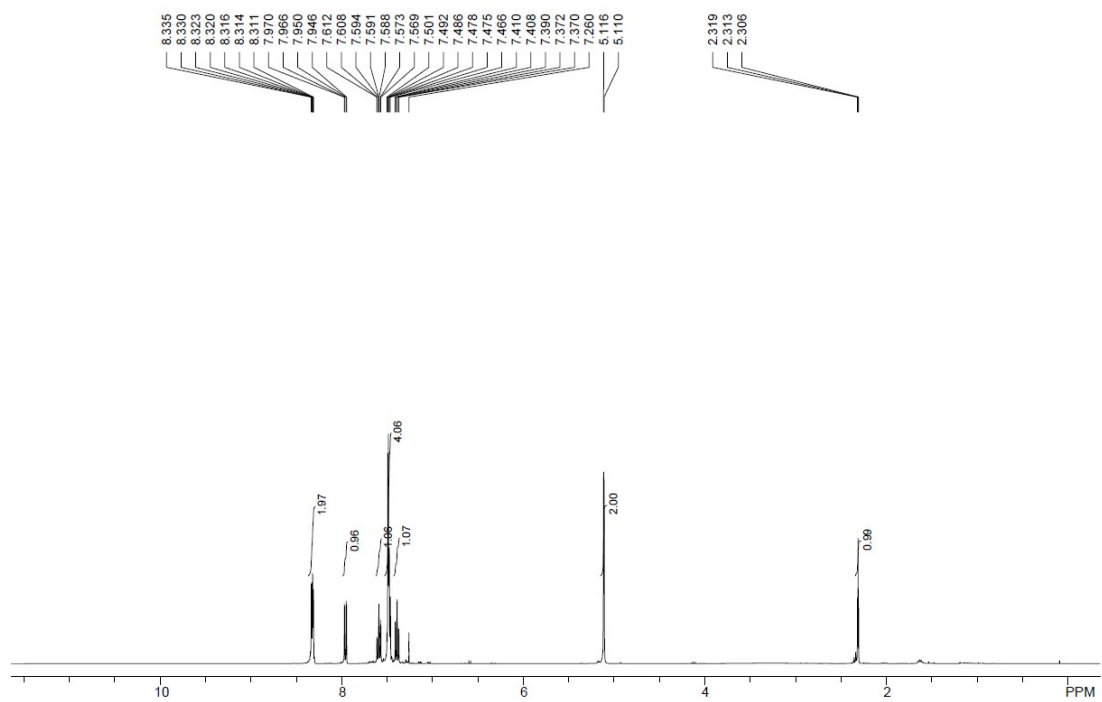


Figure S11. ^1H spectra of **3fa**

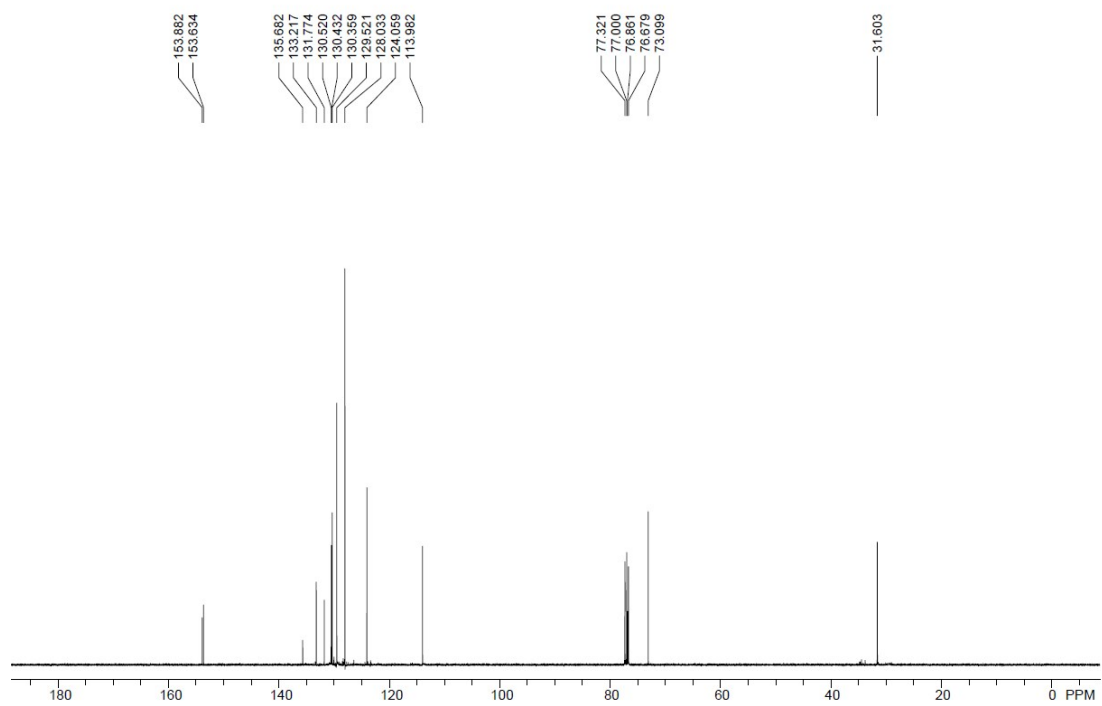


Figure S12. ^{13}C spectra of **3fa**

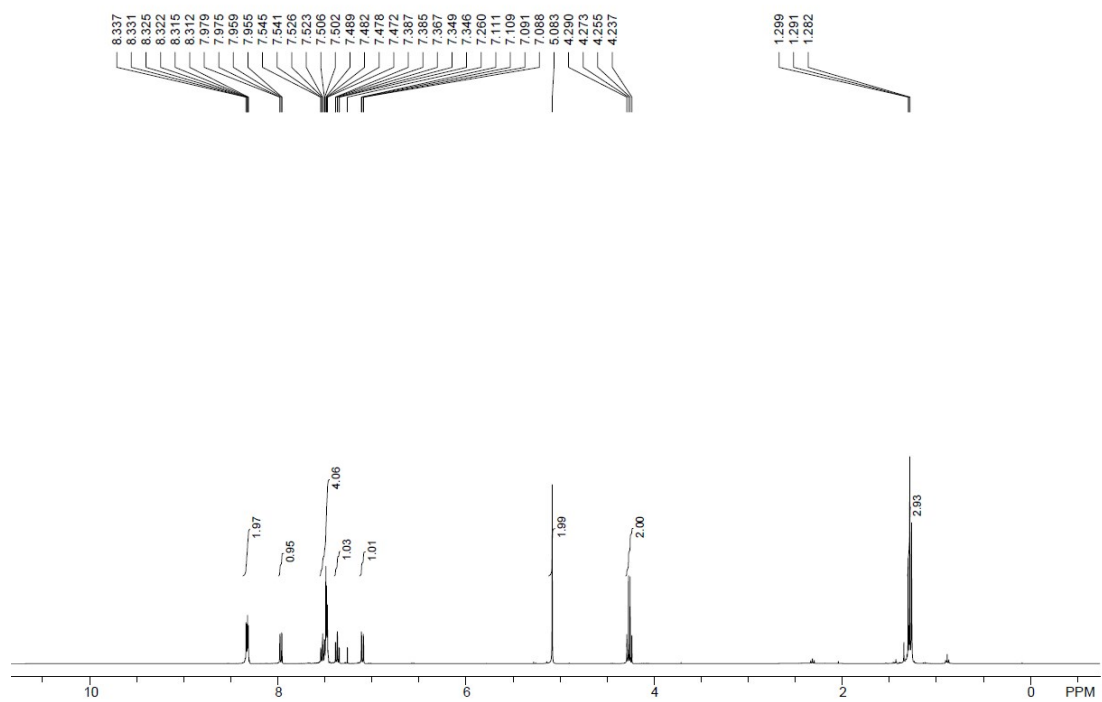


Figure S13. ¹H spectra of **3ga**

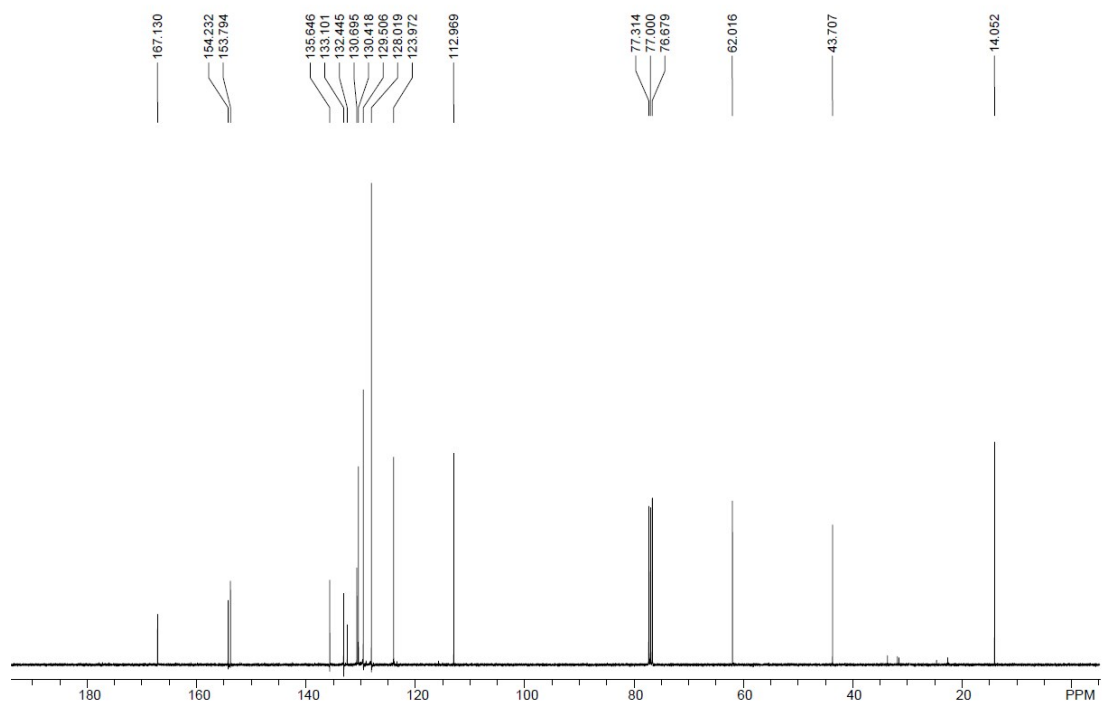


Figure S14. ¹³C spectra of **3ga**

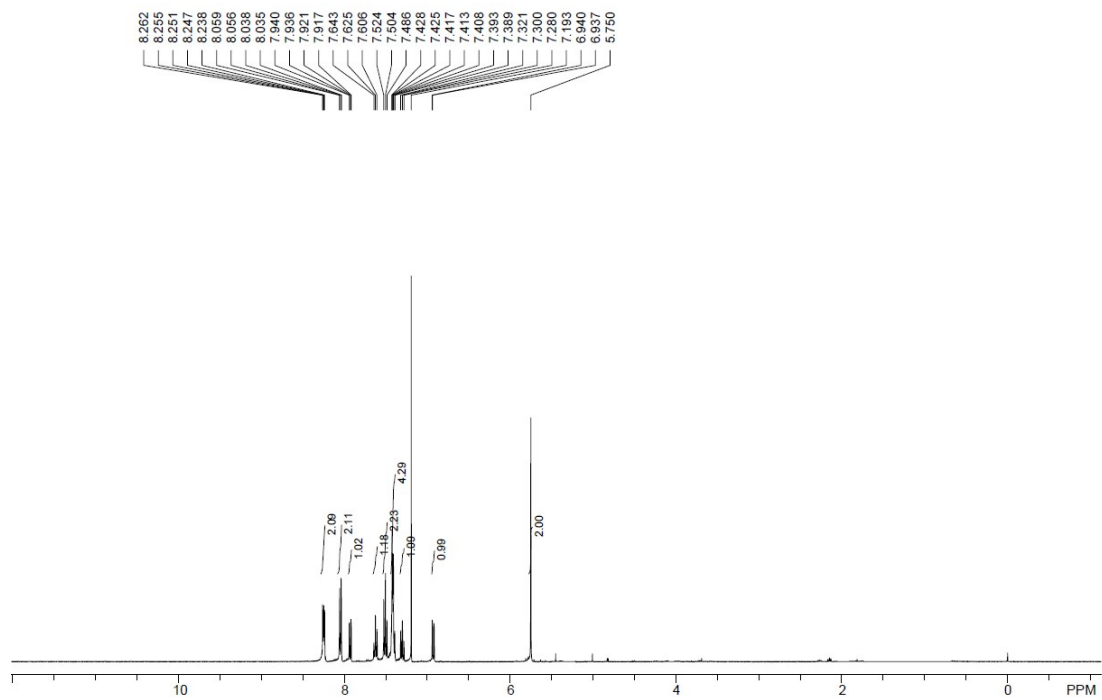


Figure S15. ^1H spectra of **3ha**

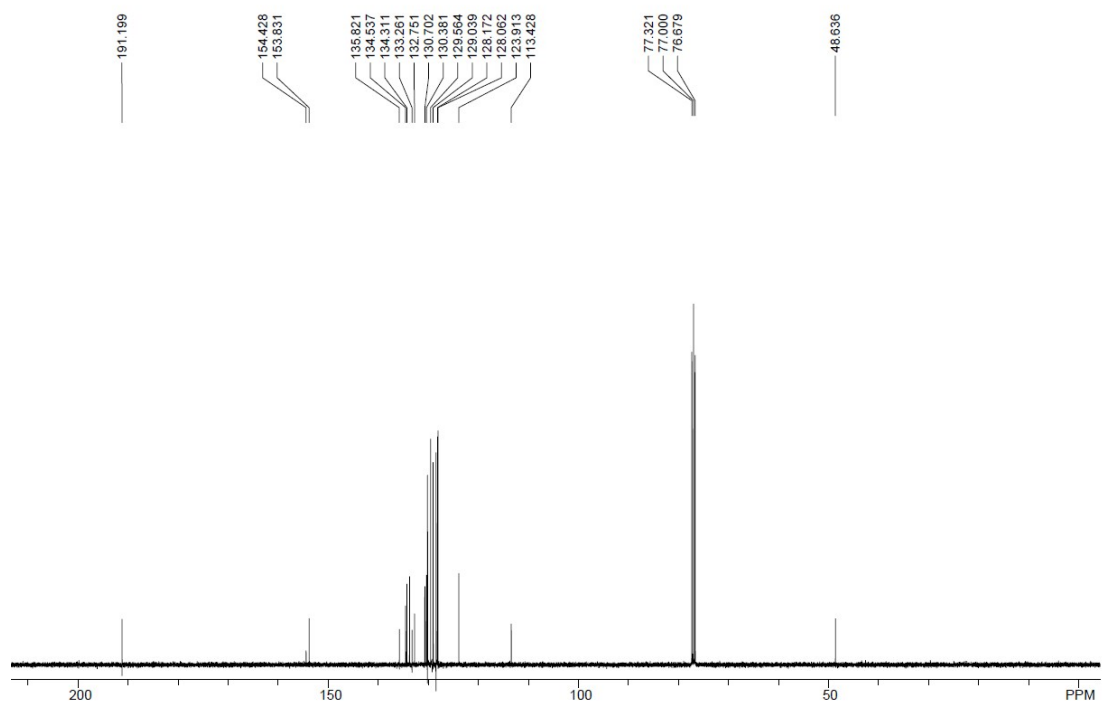


Figure S16. ^{13}C spectra of **3ha**

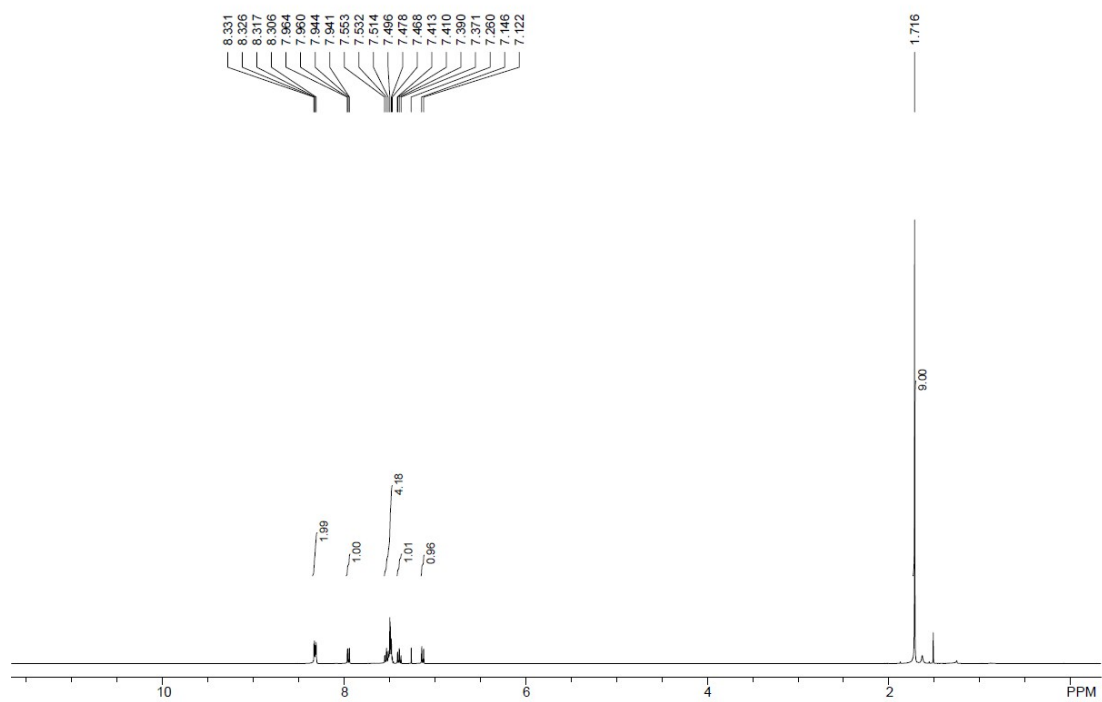


Figure S17. ^1H spectra of **3ia**

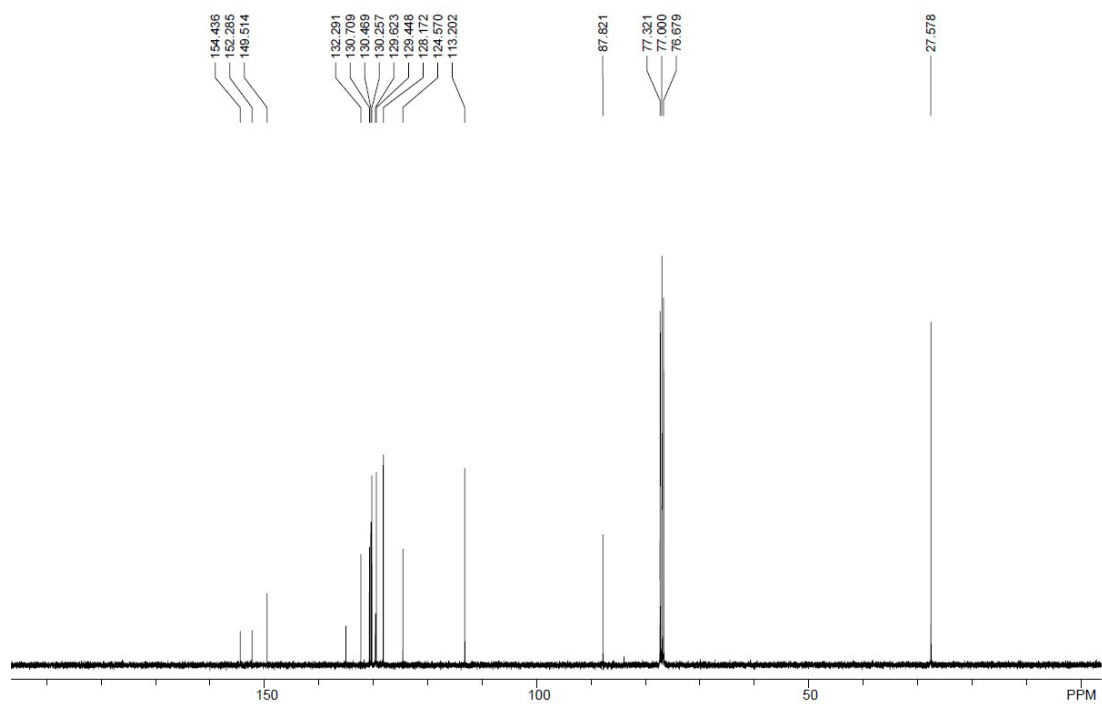


Figure S18. ^{13}C spectra of **3ia**

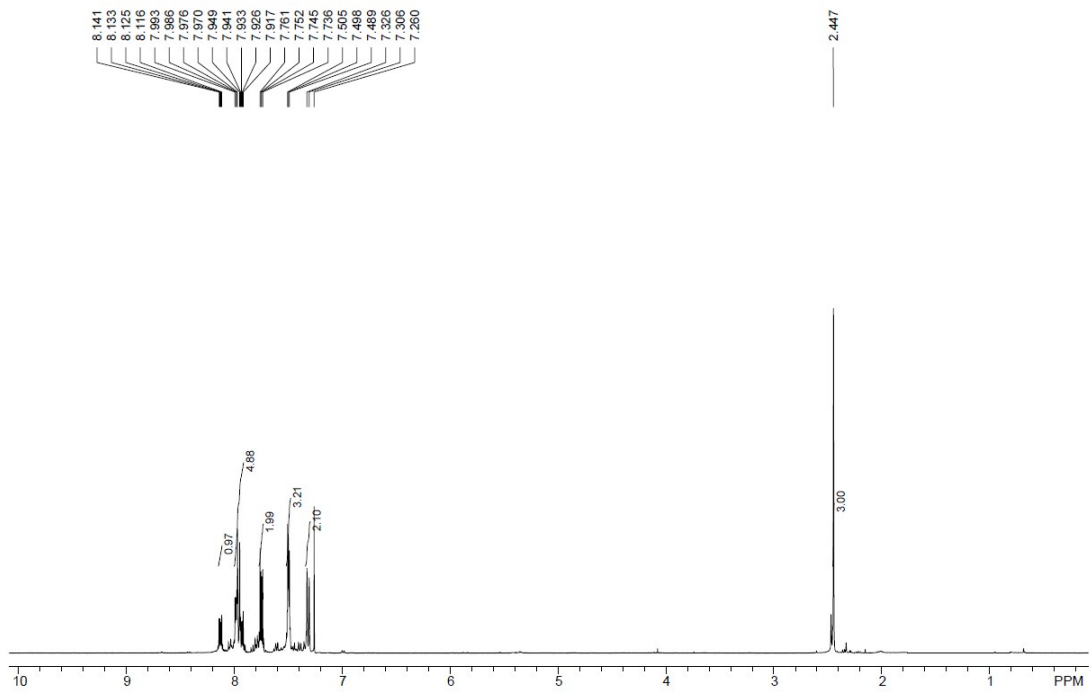


Figure S19. ^1H spectra of **3ja**

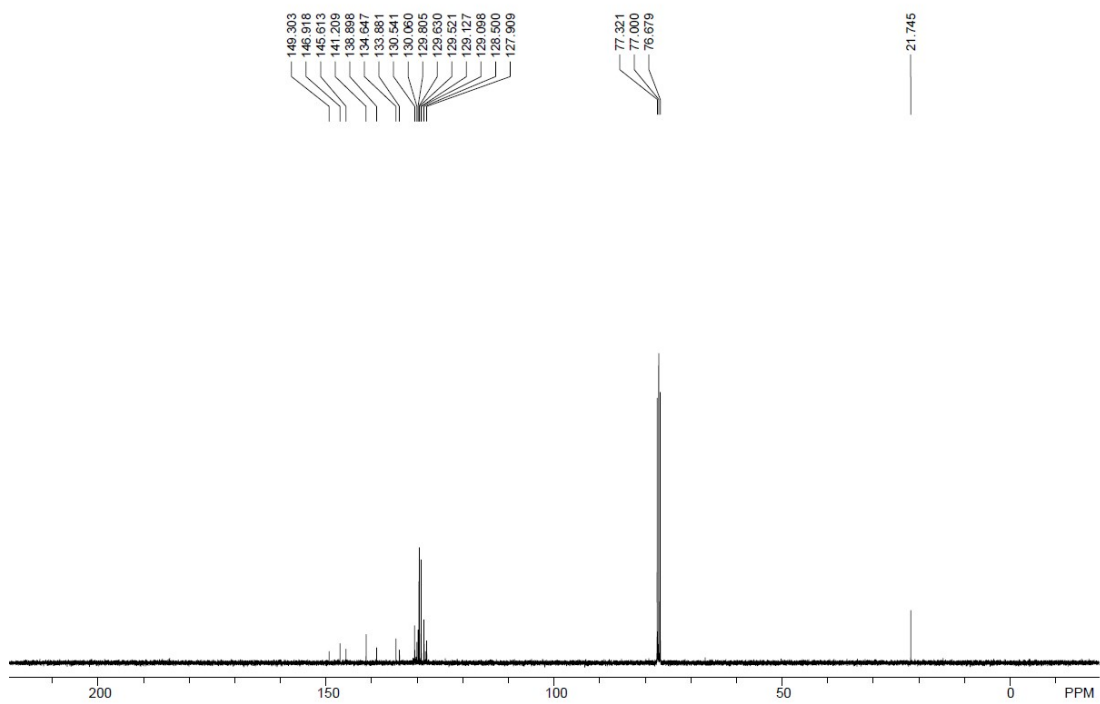


Figure S20. ^{13}C spectra of **3ja**

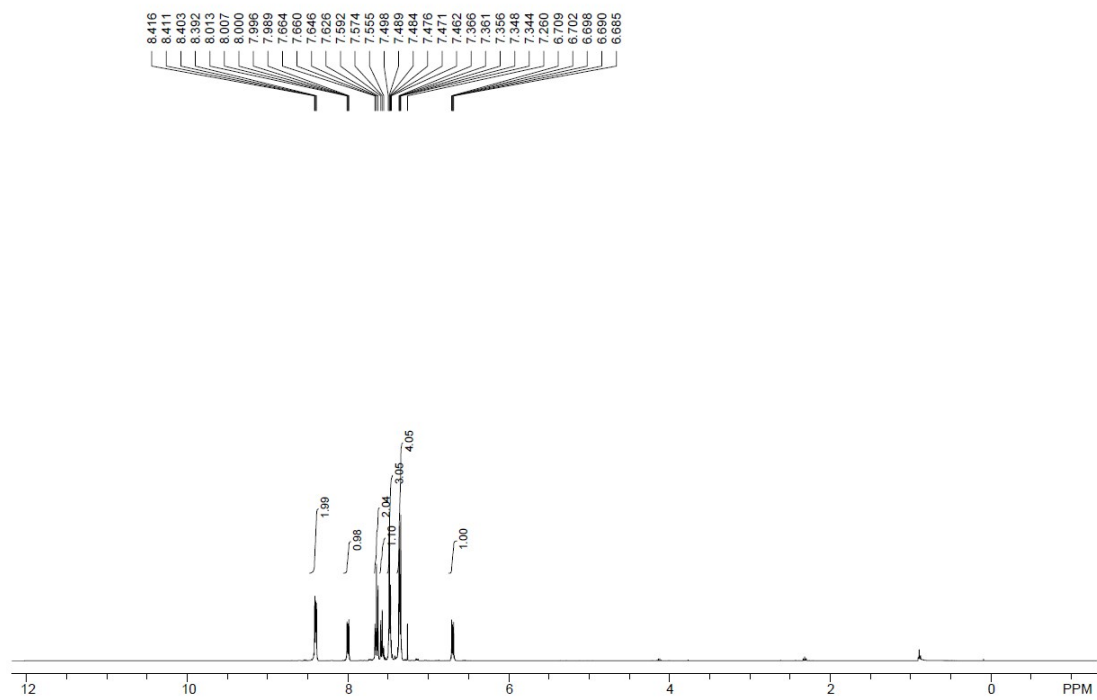


Figure S21. ¹H spectra of **3ka**

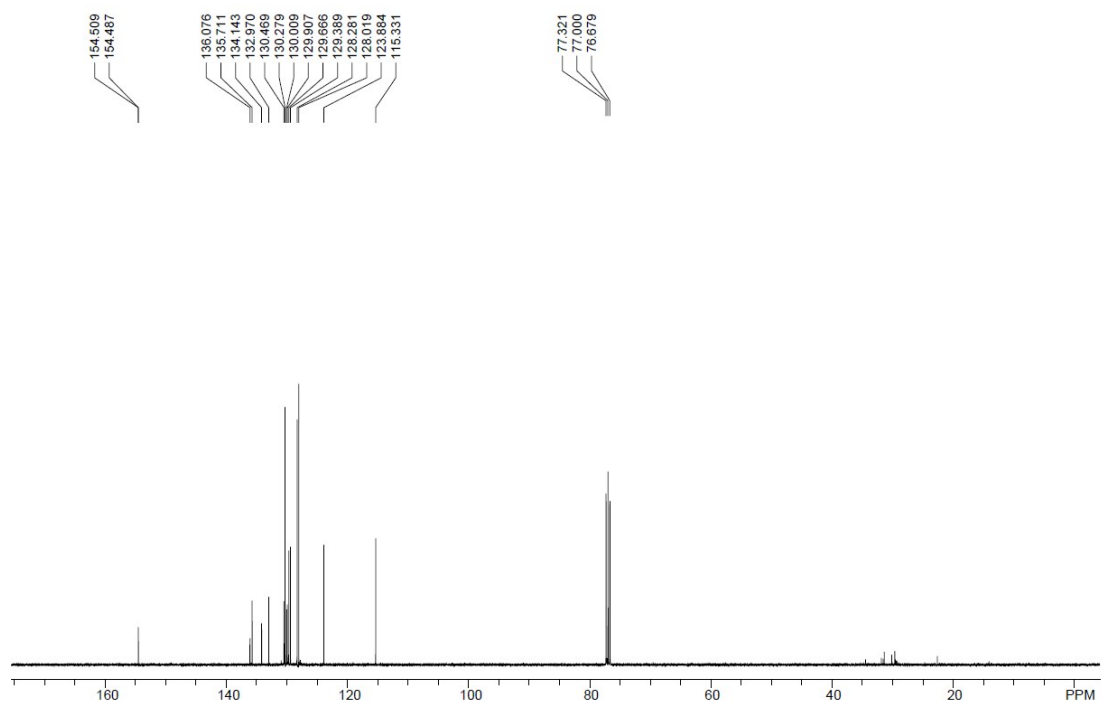


Figure S22. ¹³C spectra of **3ka**

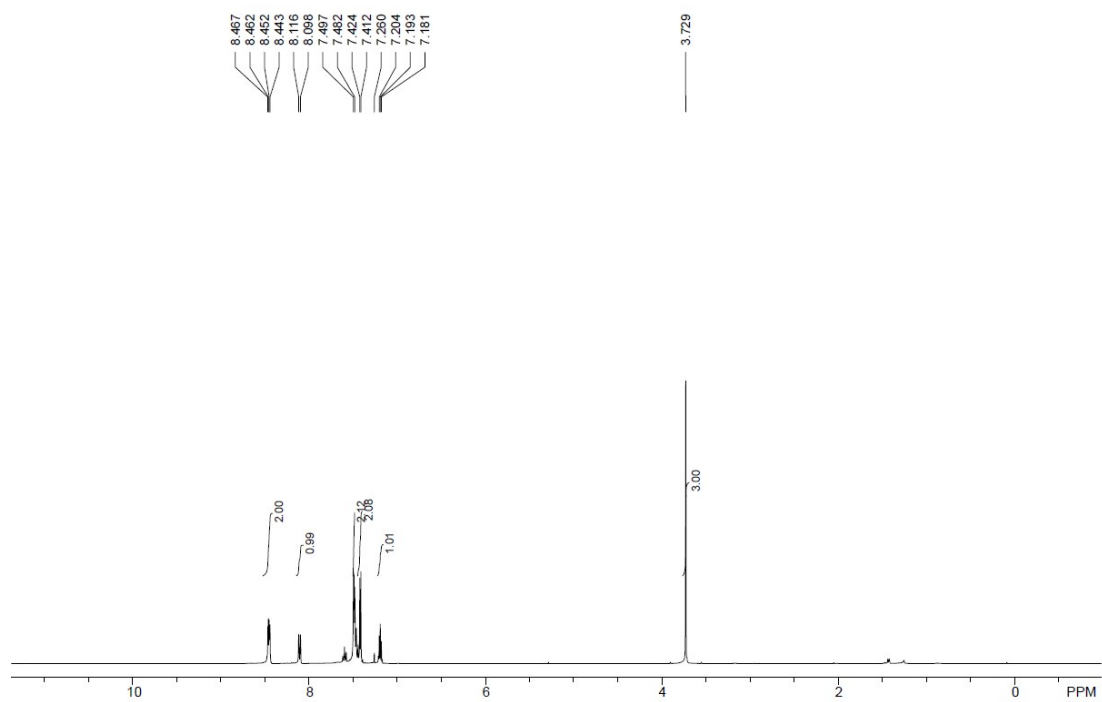


Figure S23. ^1H spectra of **31a**

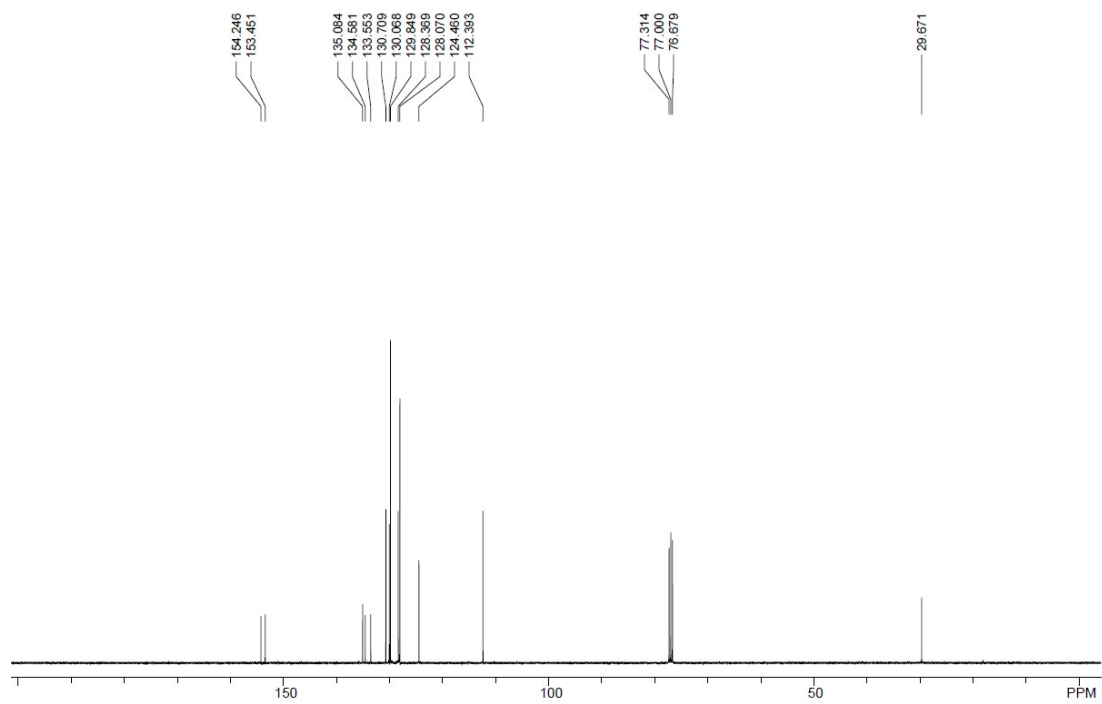


Figure S24. ^{13}C spectra of **31a**

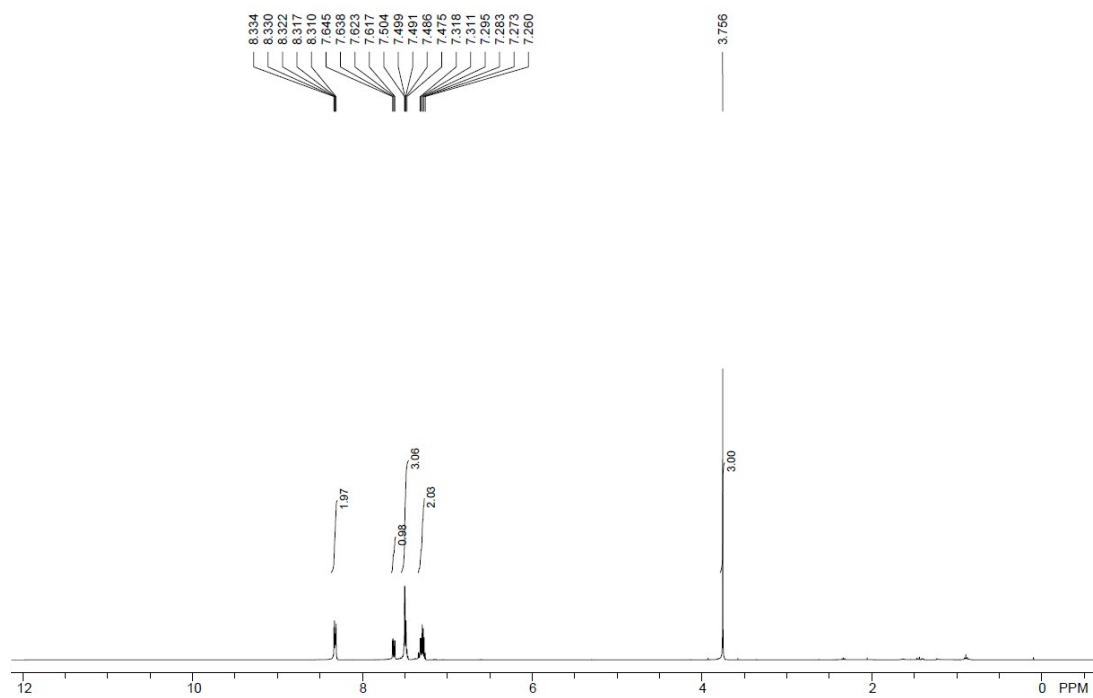


Figure S25. ^1H spectra of **3ma**

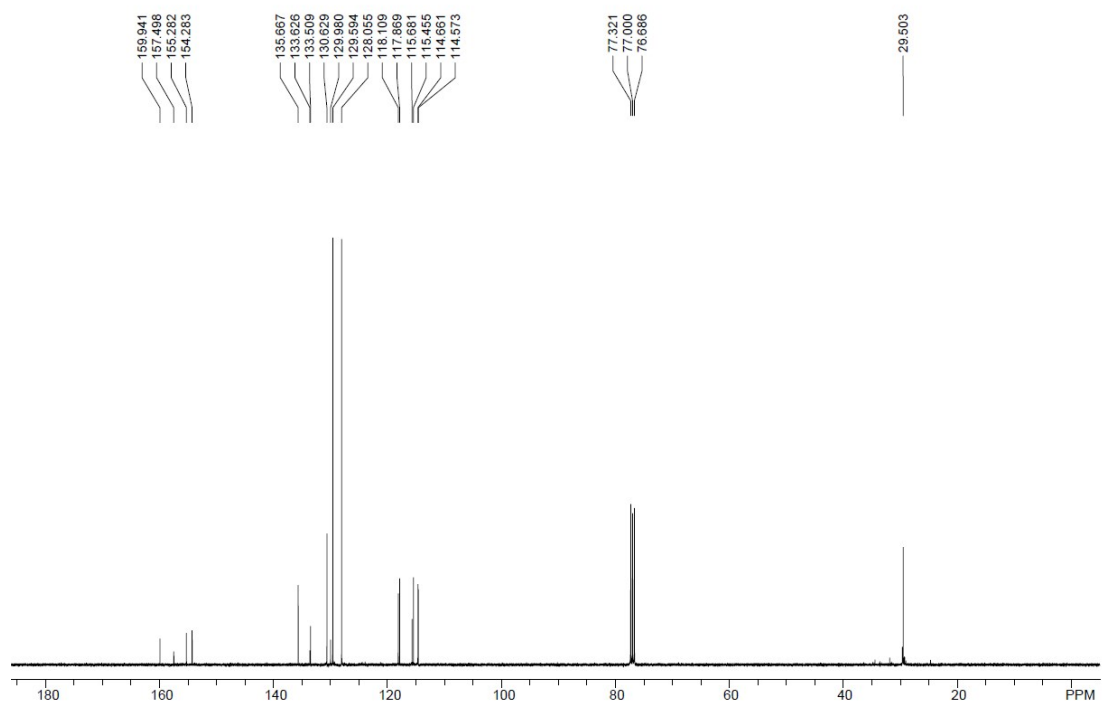


Figure S26. ^{13}C spectra of **3ma**

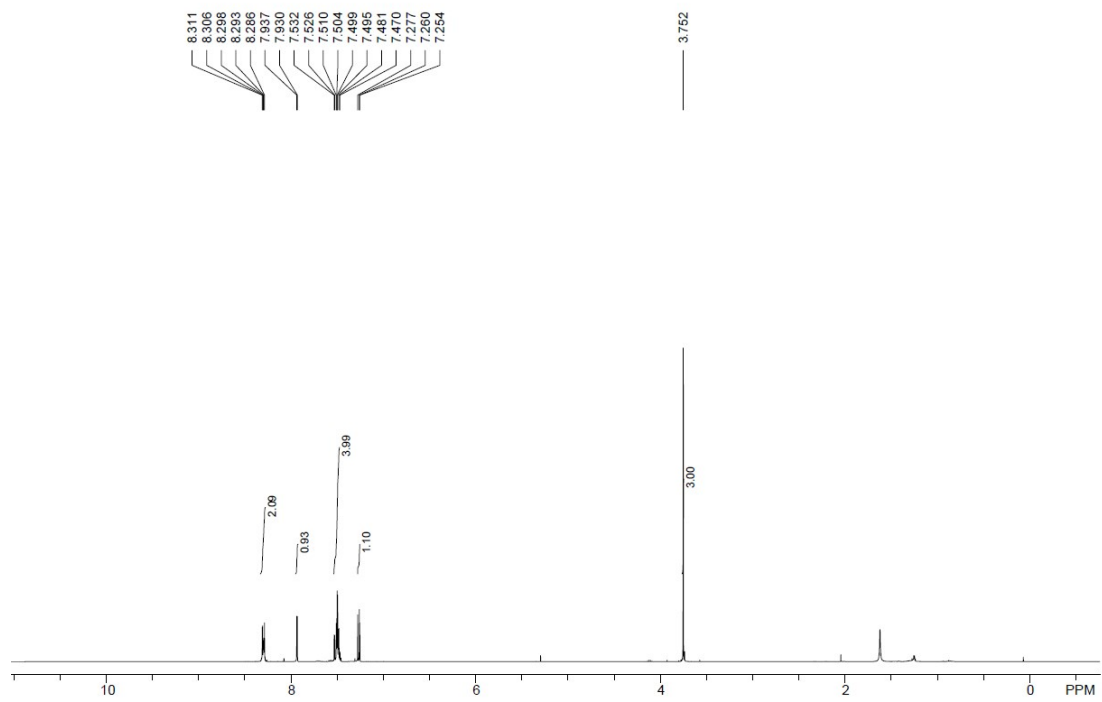


Figure S27. ^1H spectra of **3na**

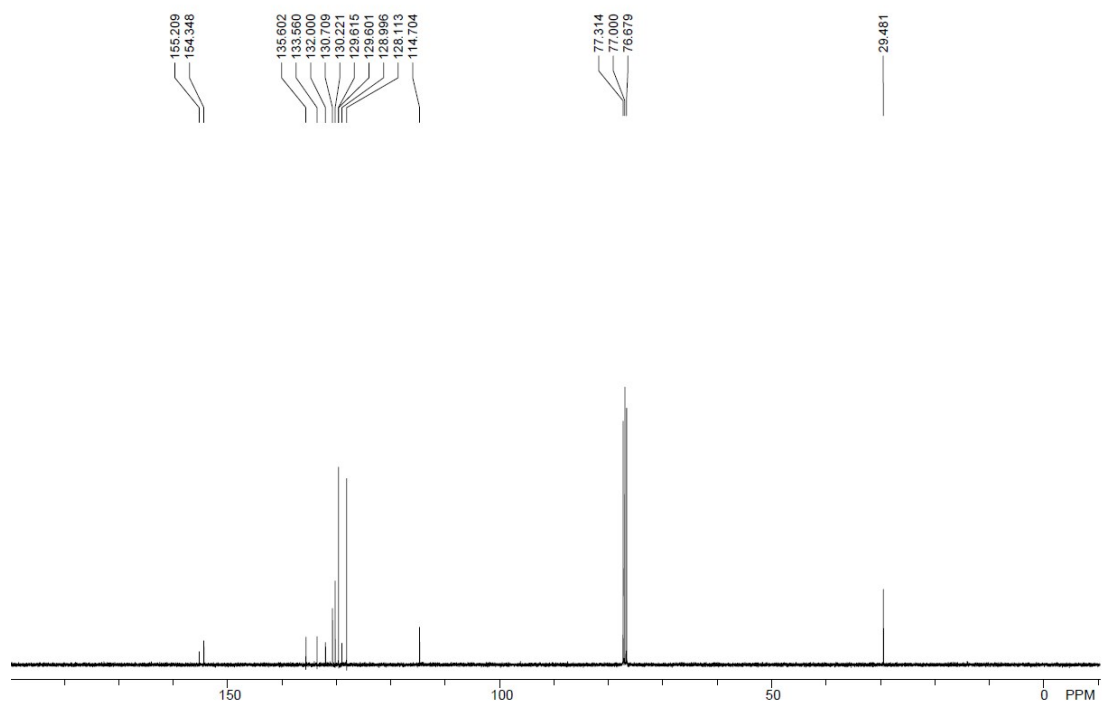


Figure S28. ^{13}C spectra of **3na**

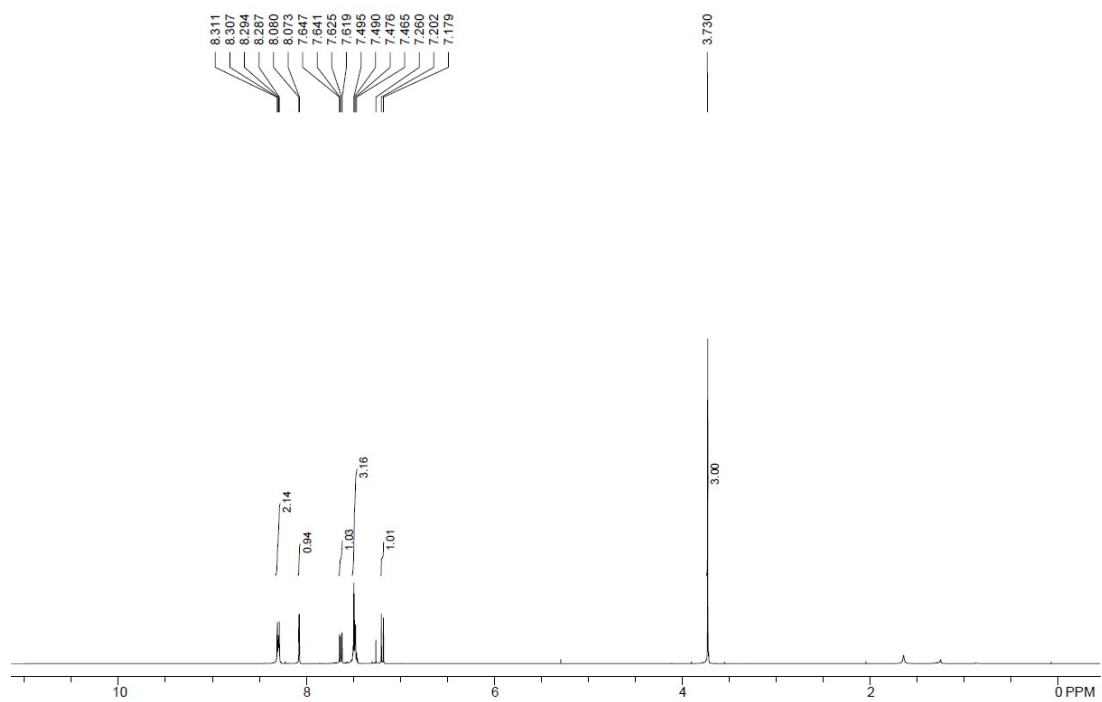


Figure S29. ¹H spectra of **30a**

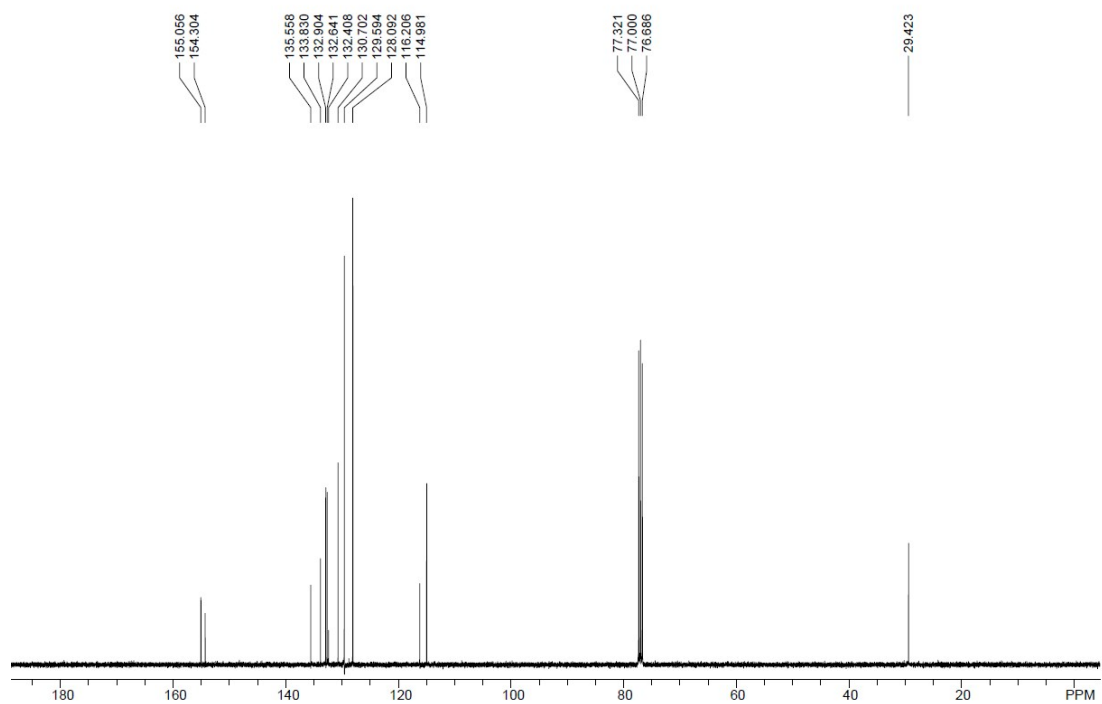


Figure S30. ¹³C spectra of **30a**

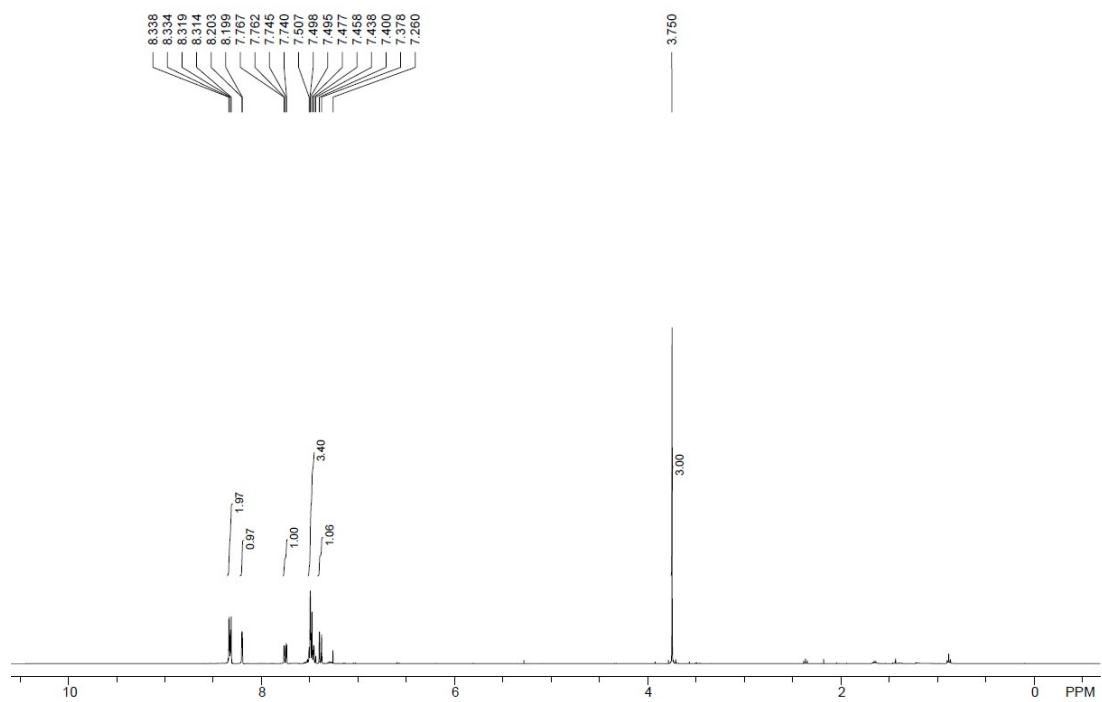


Figure S31. ^1H spectra of **3pa**

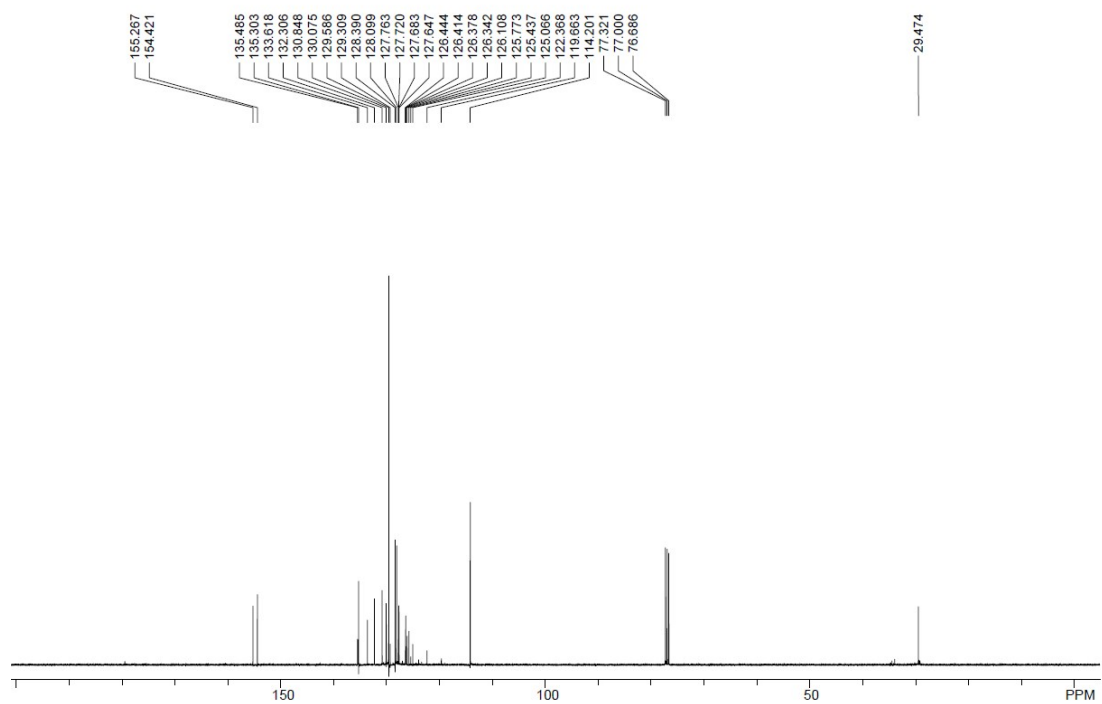


Figure S32. ^{13}C spectra of **3pa**

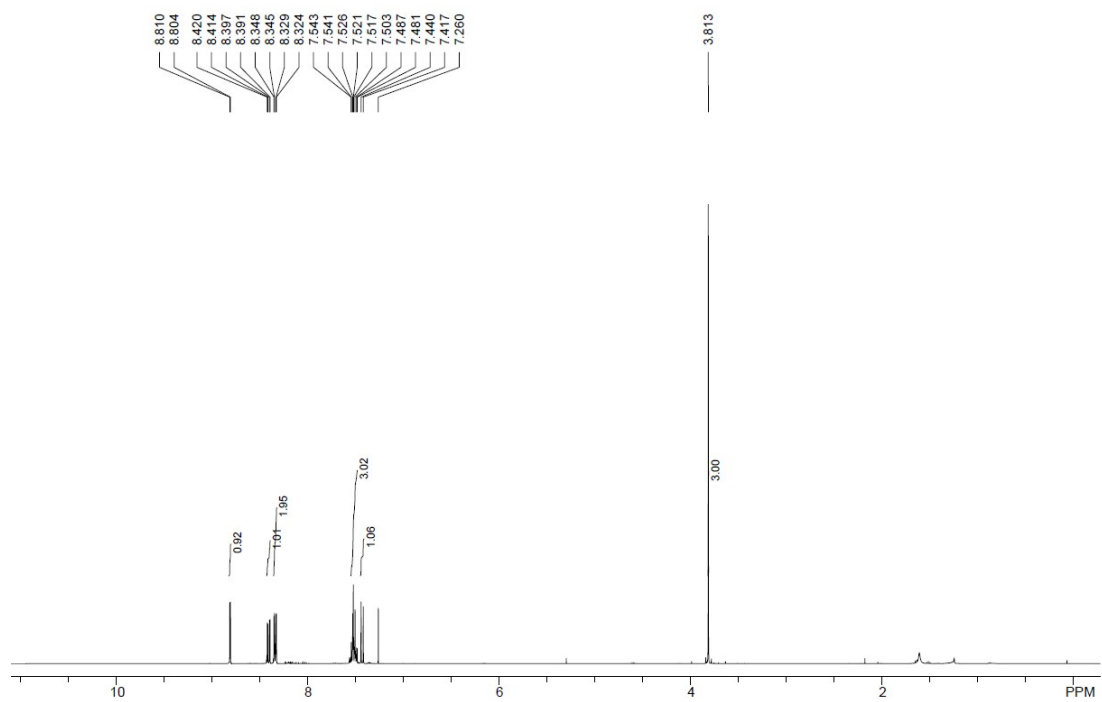


Figure S33. ^1H spectra of **3qa**

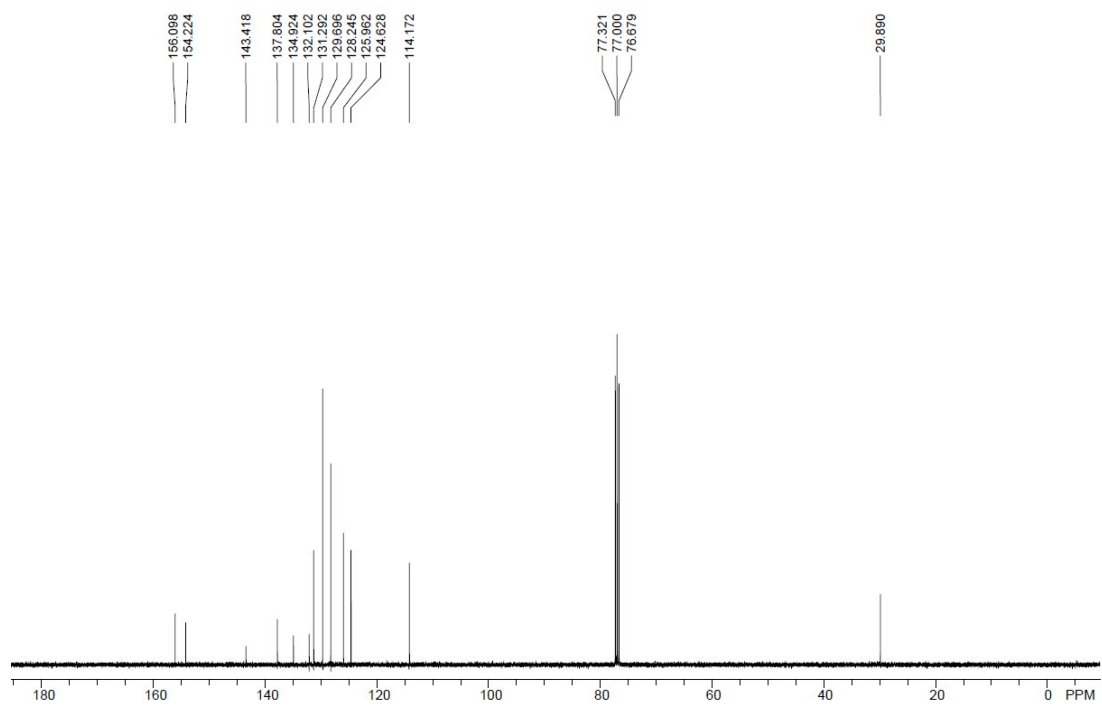


Figure S34. ^{13}C spectra of **3qa**

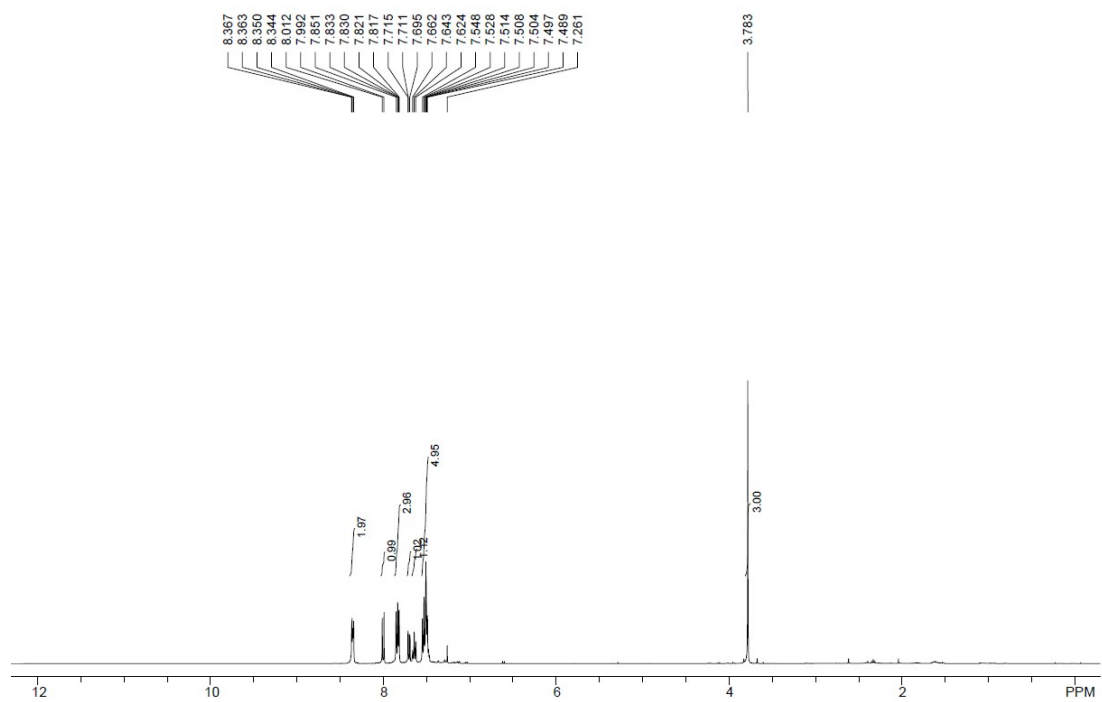


Figure S35. ¹H spectra of **3ra**

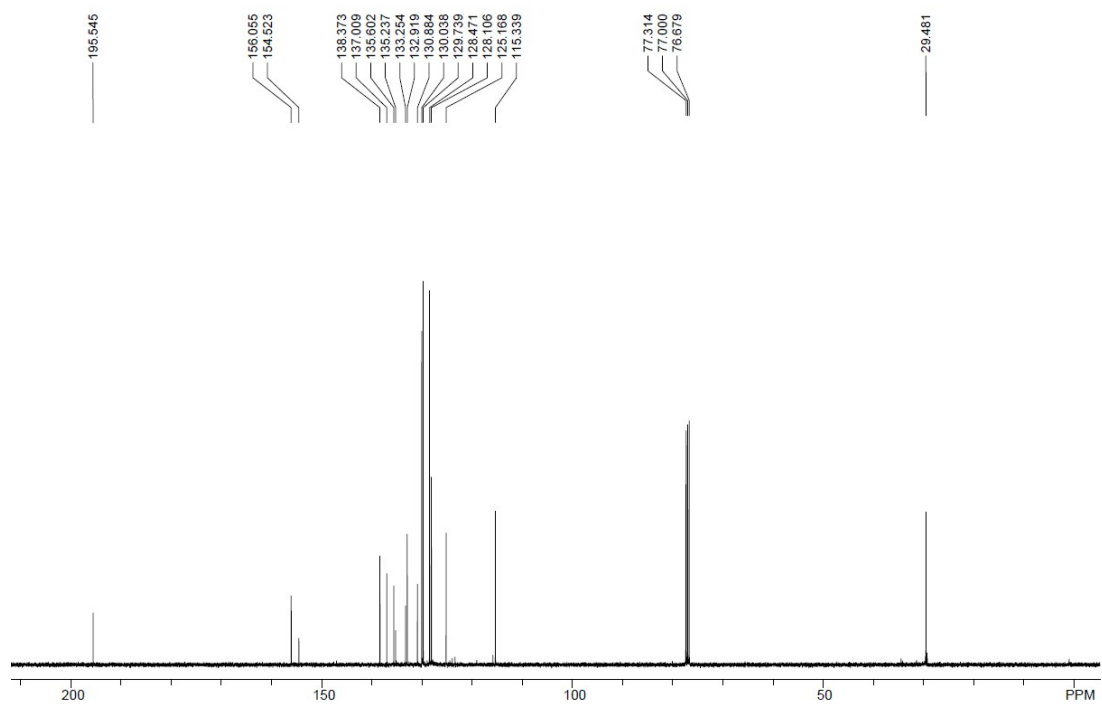


Figure S36. ¹³C spectra of **3ra**

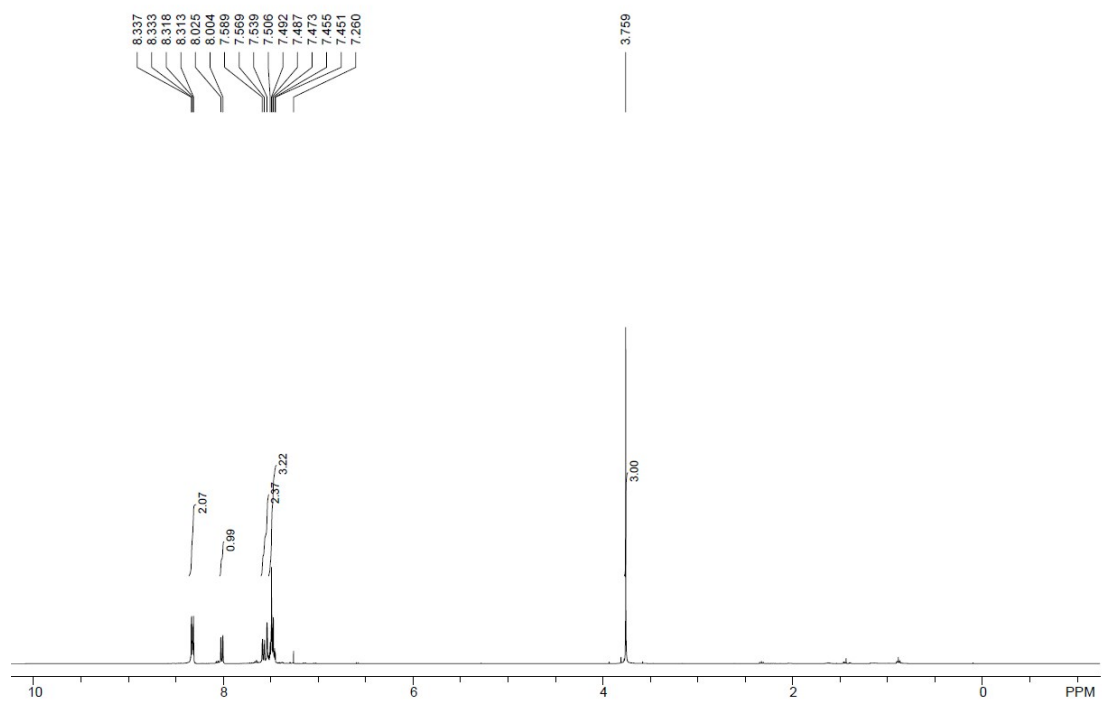


Figure S37. ^1H spectra of **3sa**

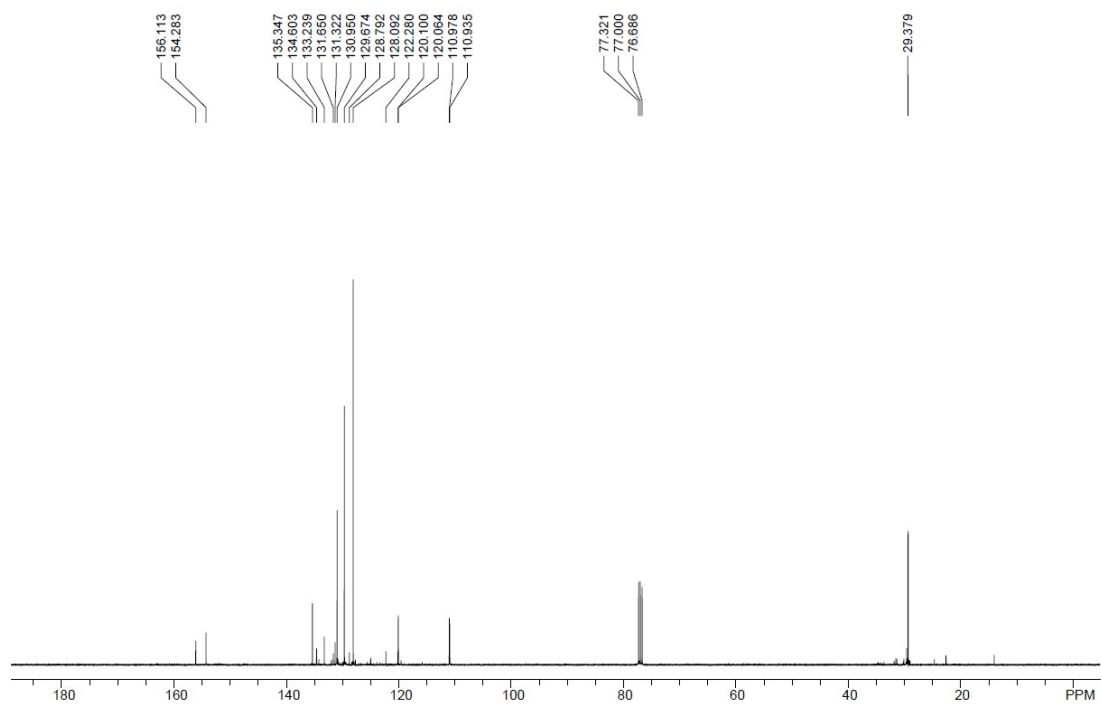


Figure S38. ^{13}C spectra of **3sa**

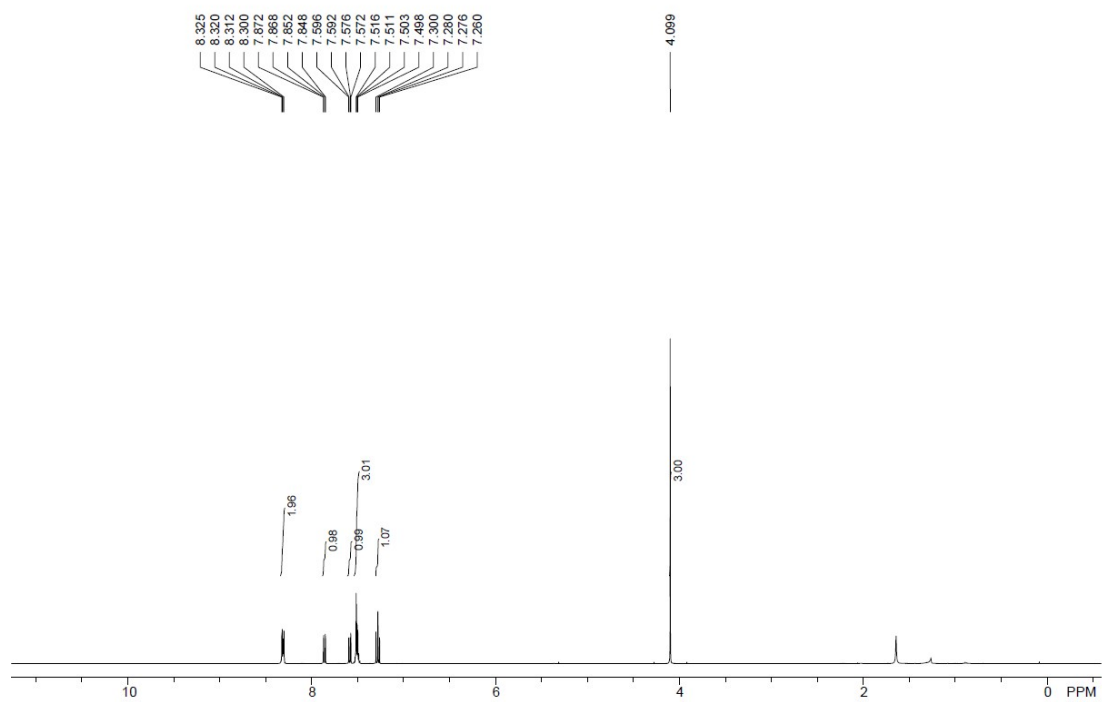


Figure S39. ^1H spectra of **3ta**

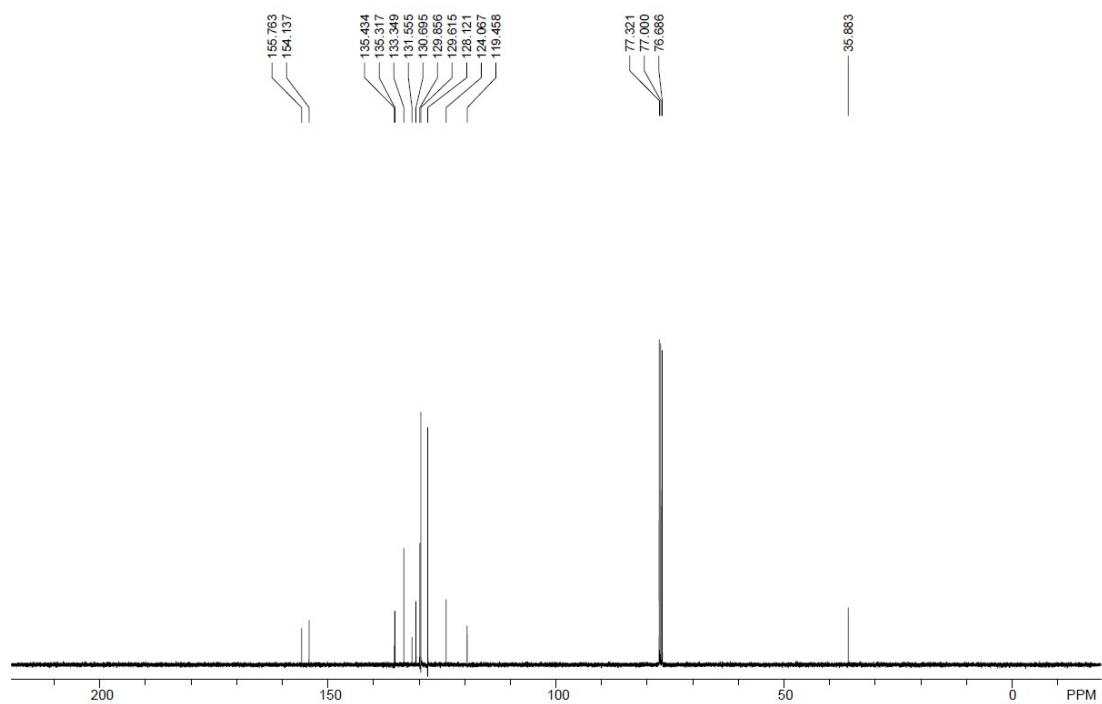


Figure S40. ^{13}C spectra of **3ta**

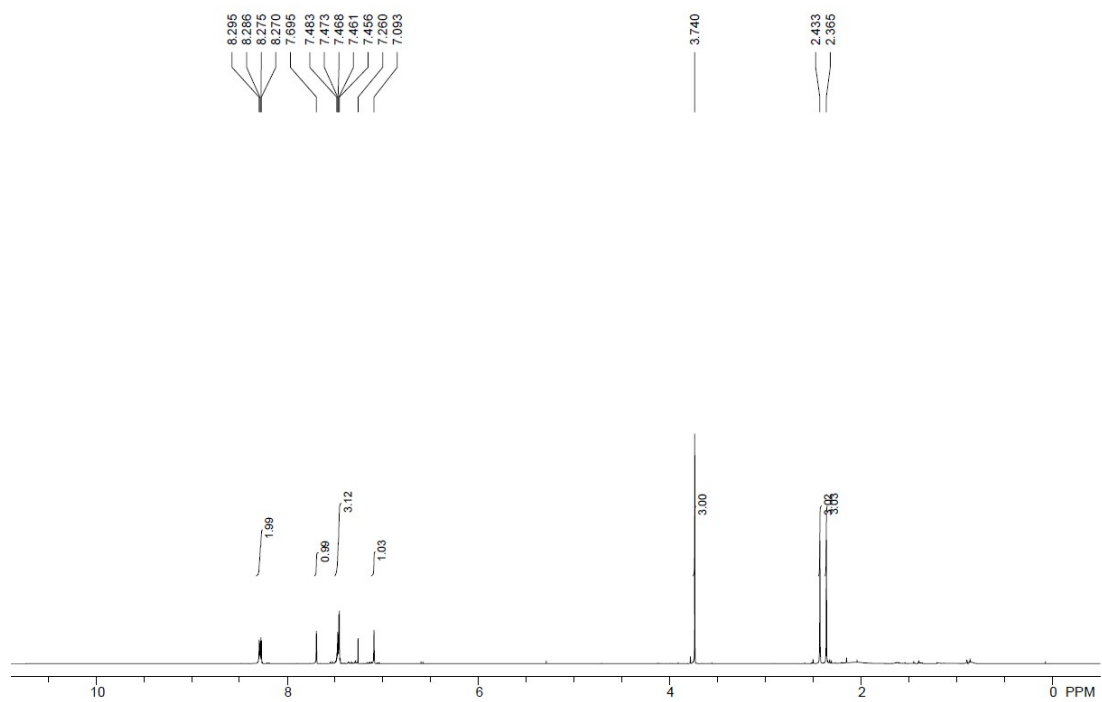


Figure S41. ^1H spectra of **3ua**

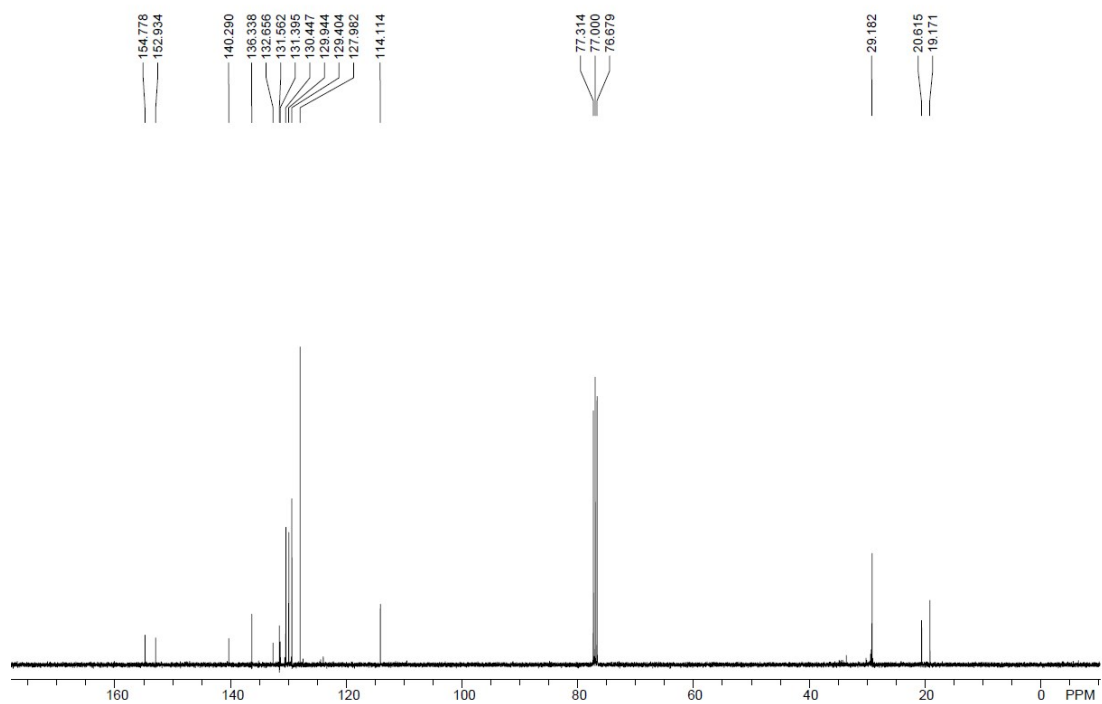


Figure S42. ^{13}C spectra of **3ua**

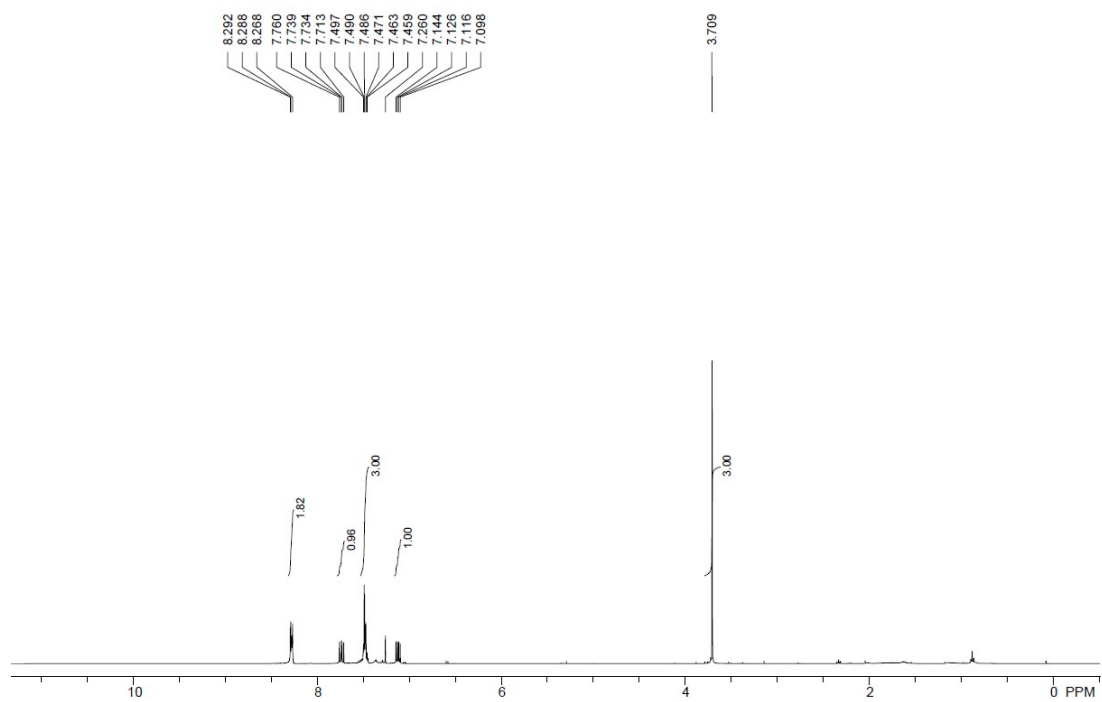


Figure S43. ^1H spectra of **3va**

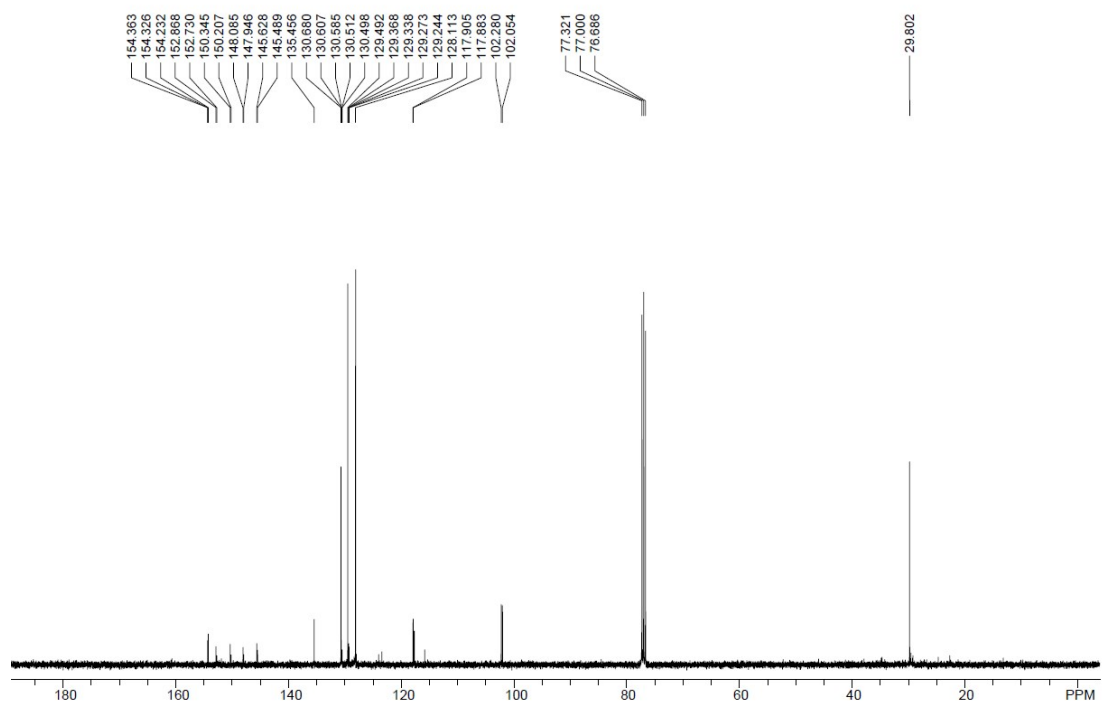


Figure S44. ^{13}C spectra of **3va**

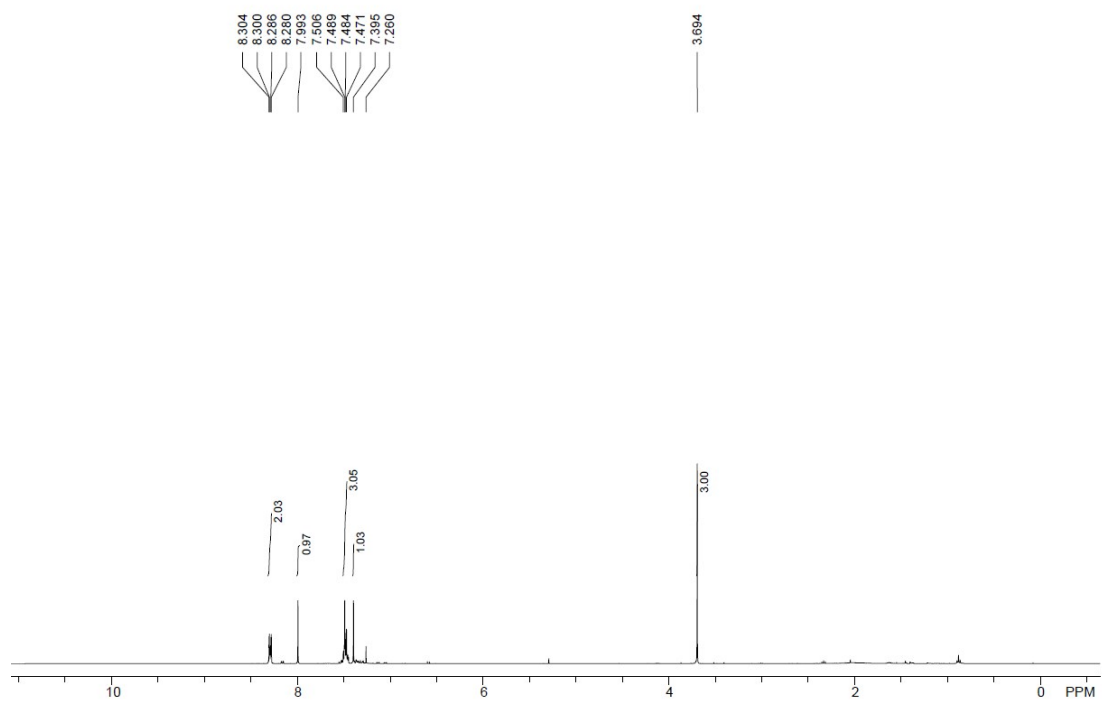


Figure S45. ^1H spectra of **3wa**

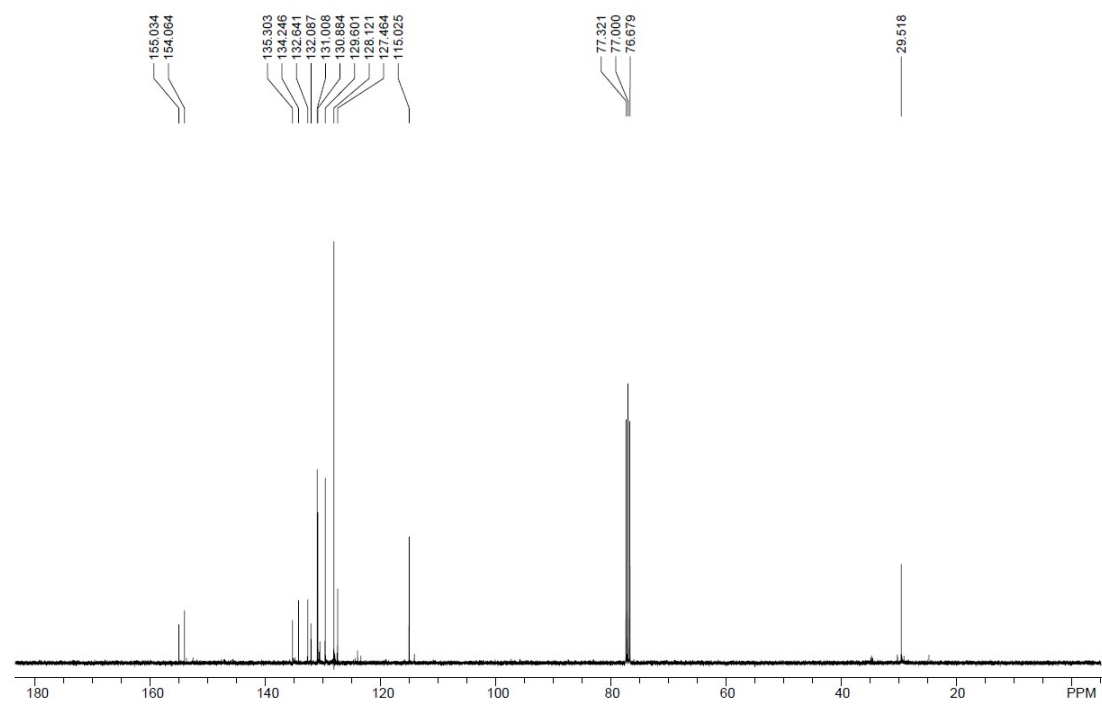


Figure S46. ^{13}C spectra of **3wa**

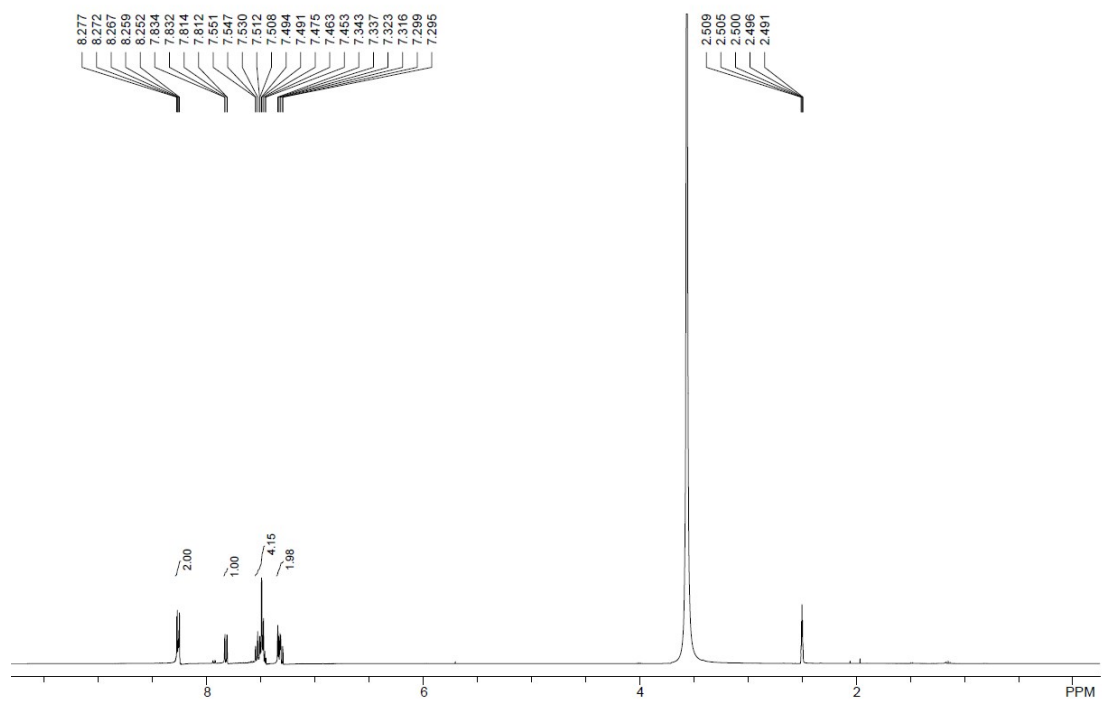


Figure S47. ¹H spectra of **3xa**

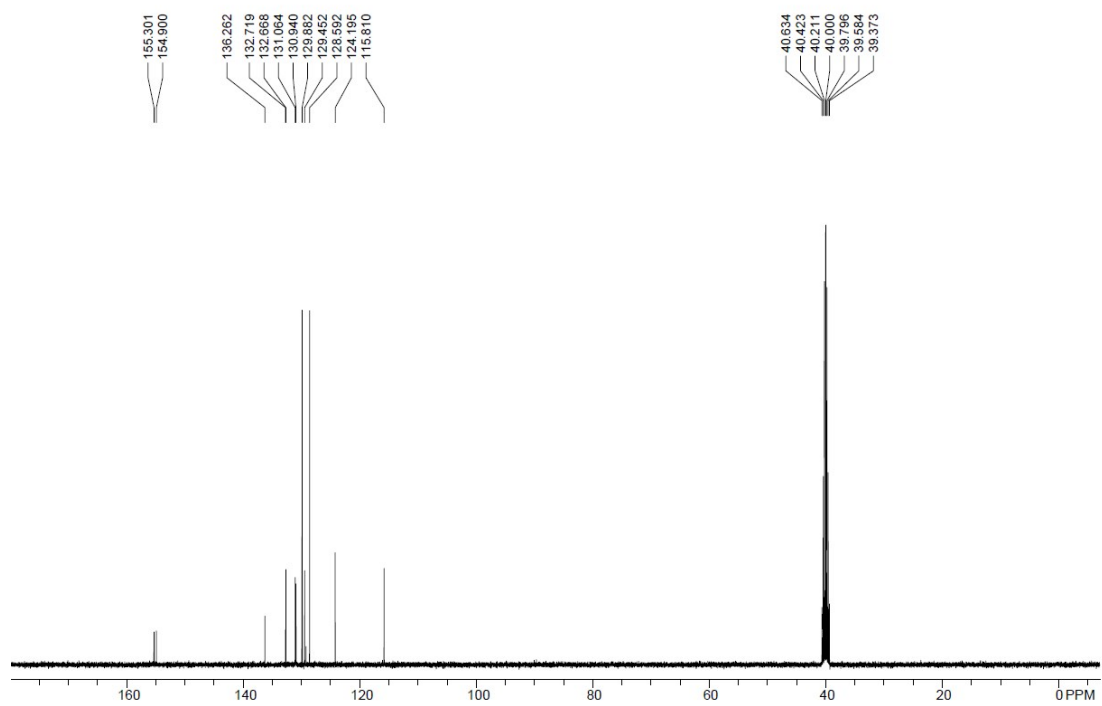


Figure S48. ¹³C spectra of **3xa**

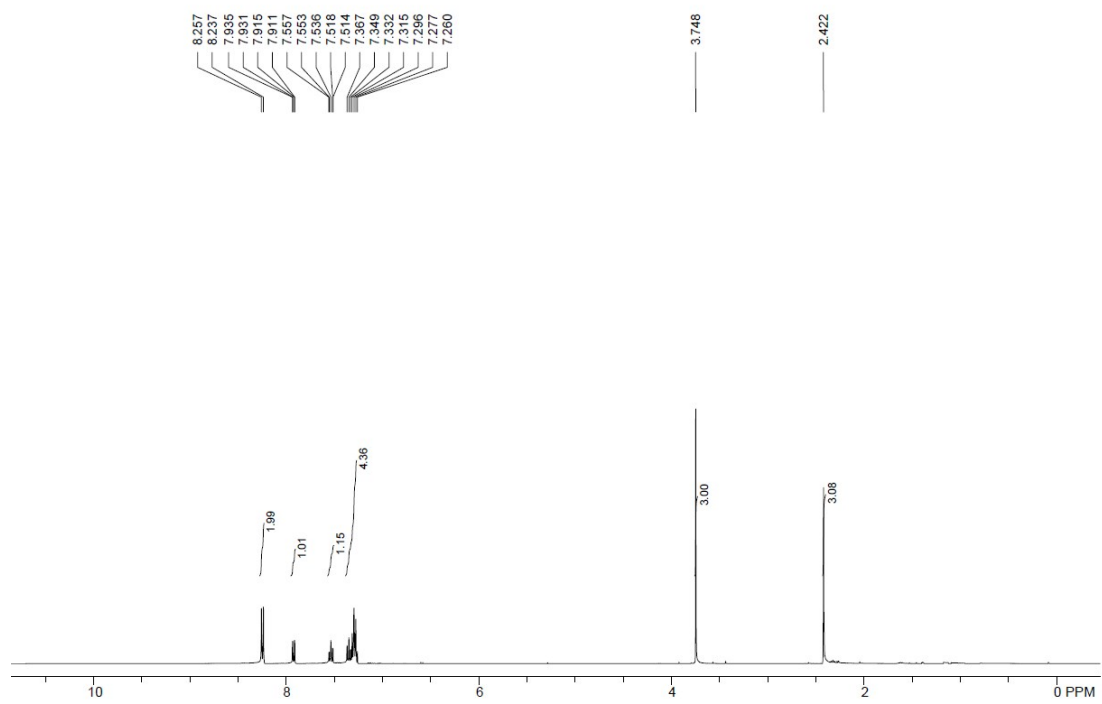


Figure S49. ^1H spectra of **3ab**

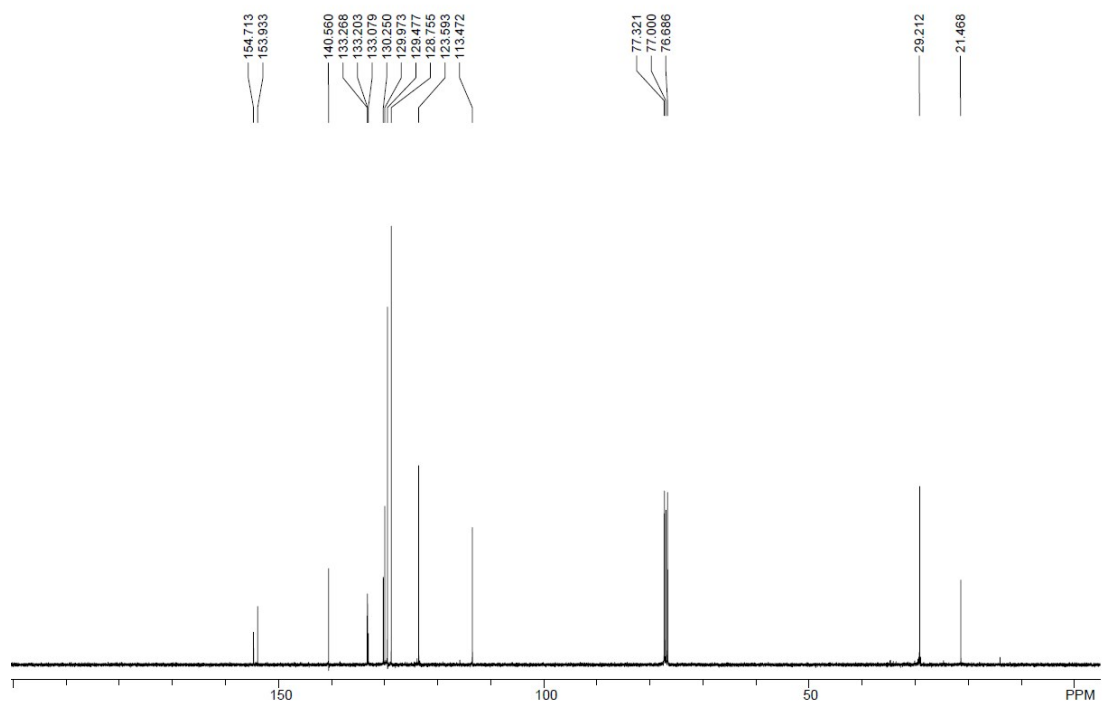


Figure S50. ^{13}C spectra of **3ab**

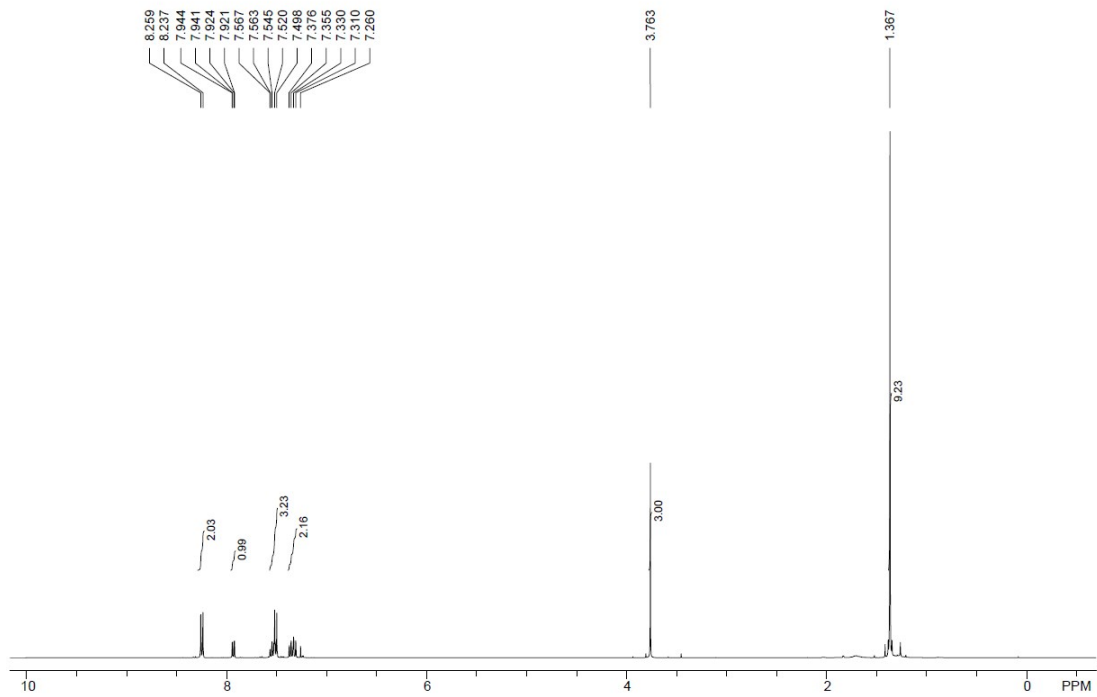


Figure S51. ^1H spectra of **3ac**

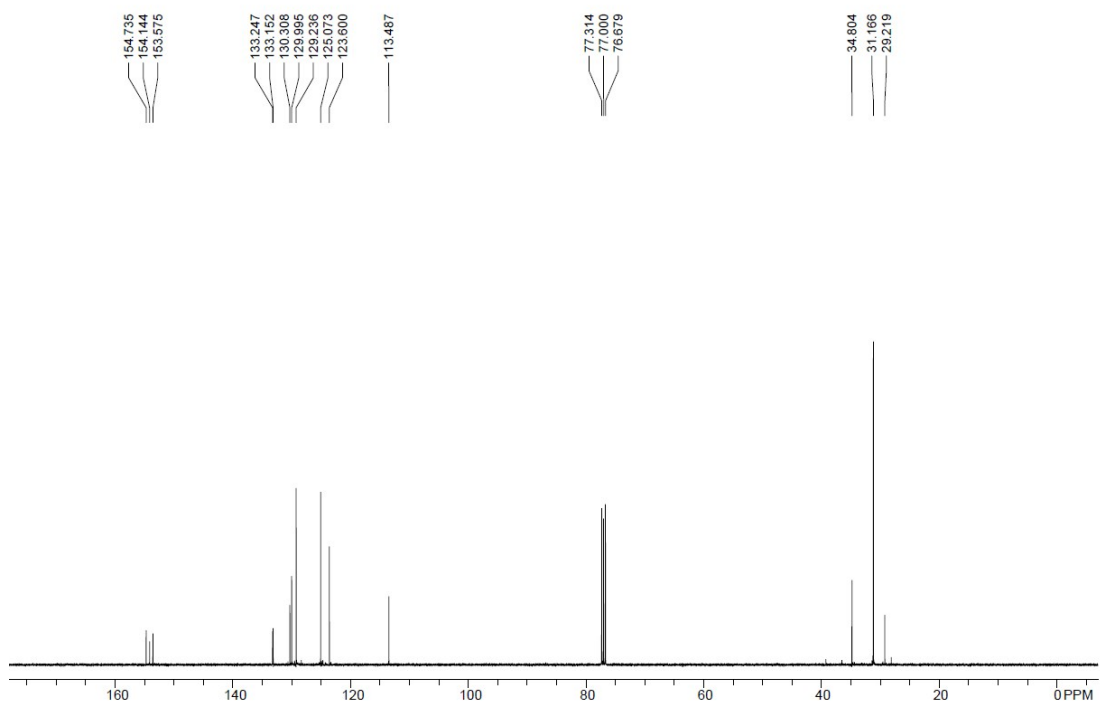


Figure S52. ^{13}C spectra of **3ac**

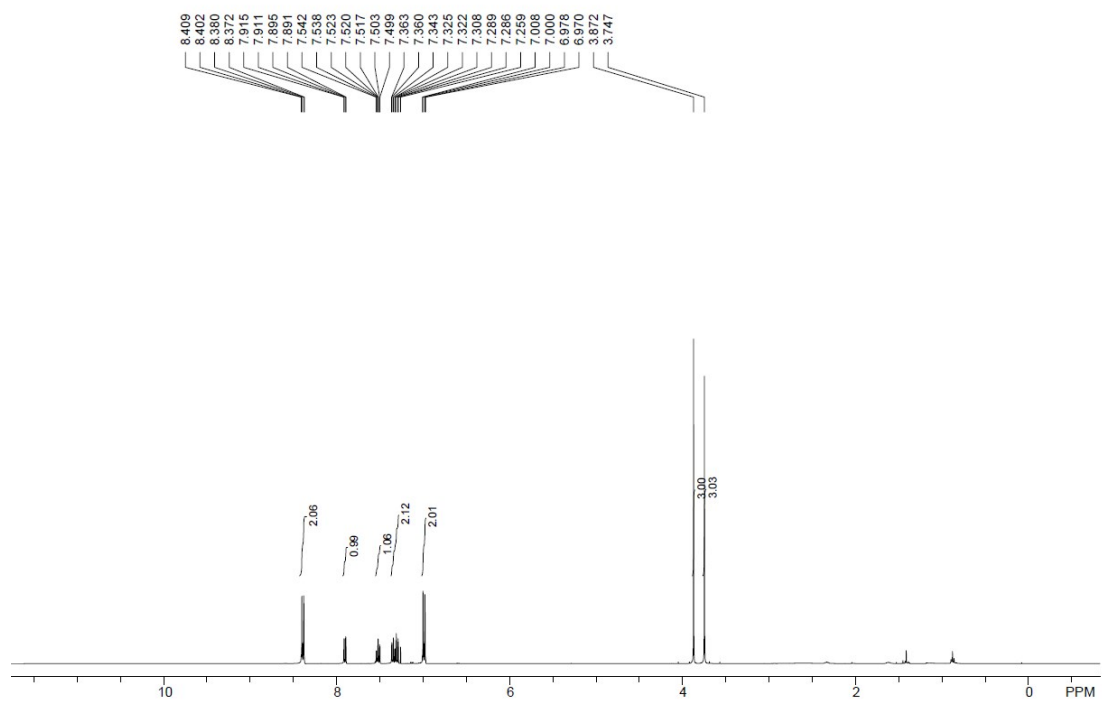


Figure S53. ^1H spectra of **3ad**

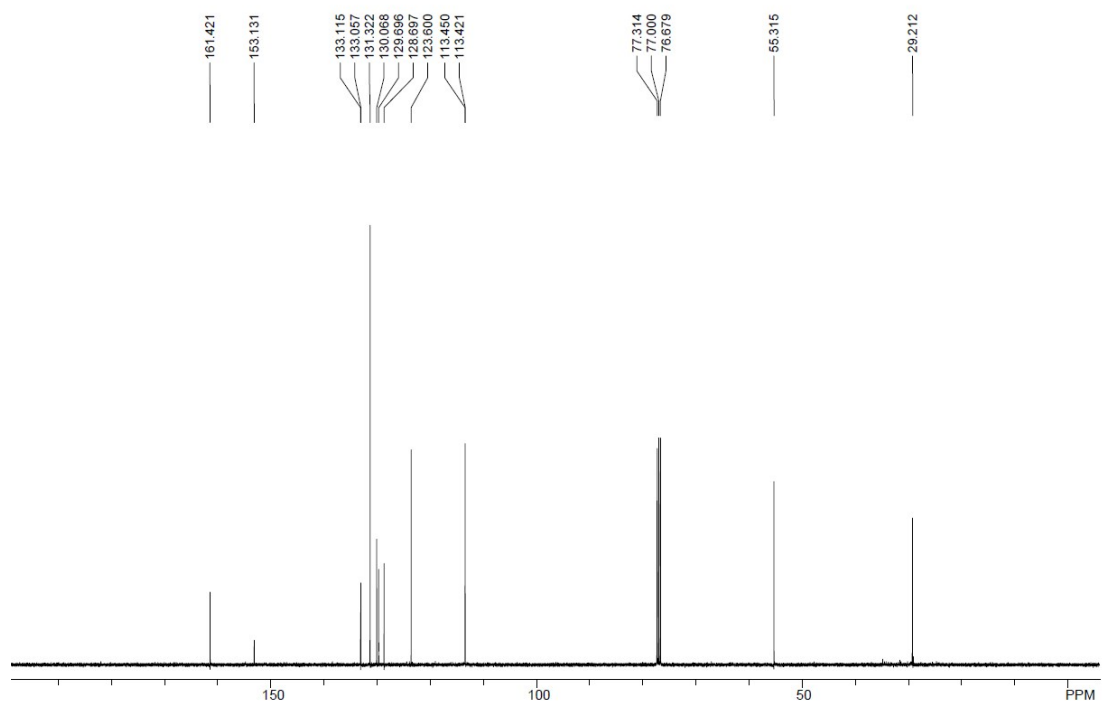


Figure S54. ^{13}C spectra of **3ad**

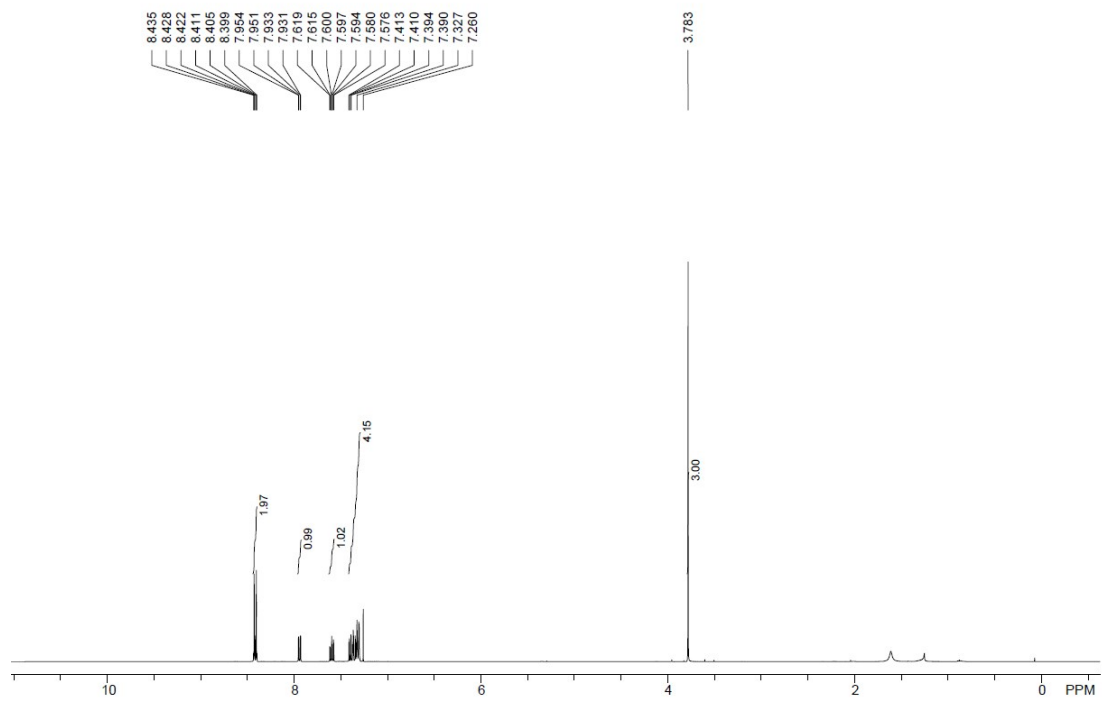


Figure S55. ^1H spectra of **3ae**

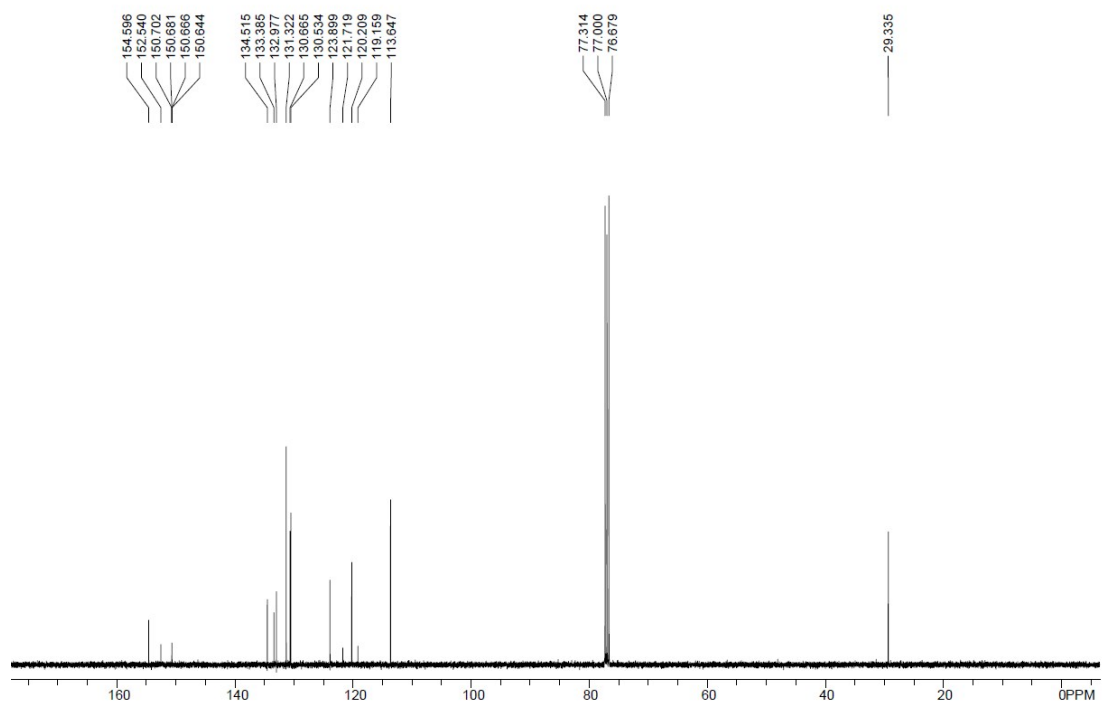


Figure S56. ^{13}C spectra of **3ae**

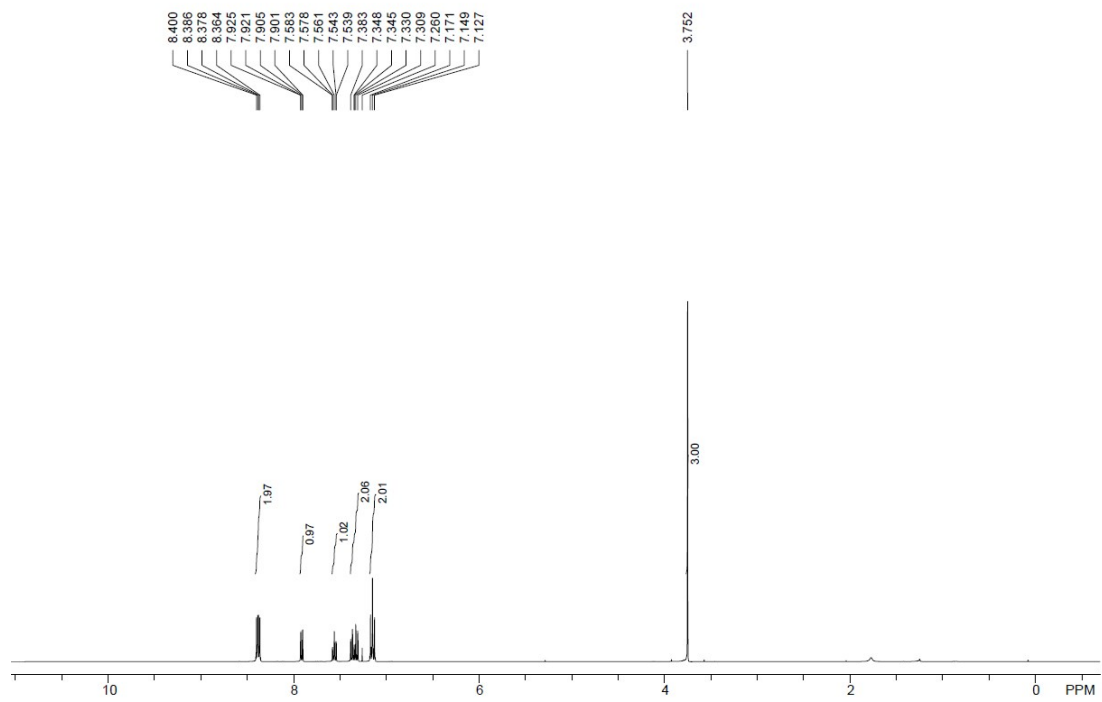


Figure S57. ^1H spectra of **3af**

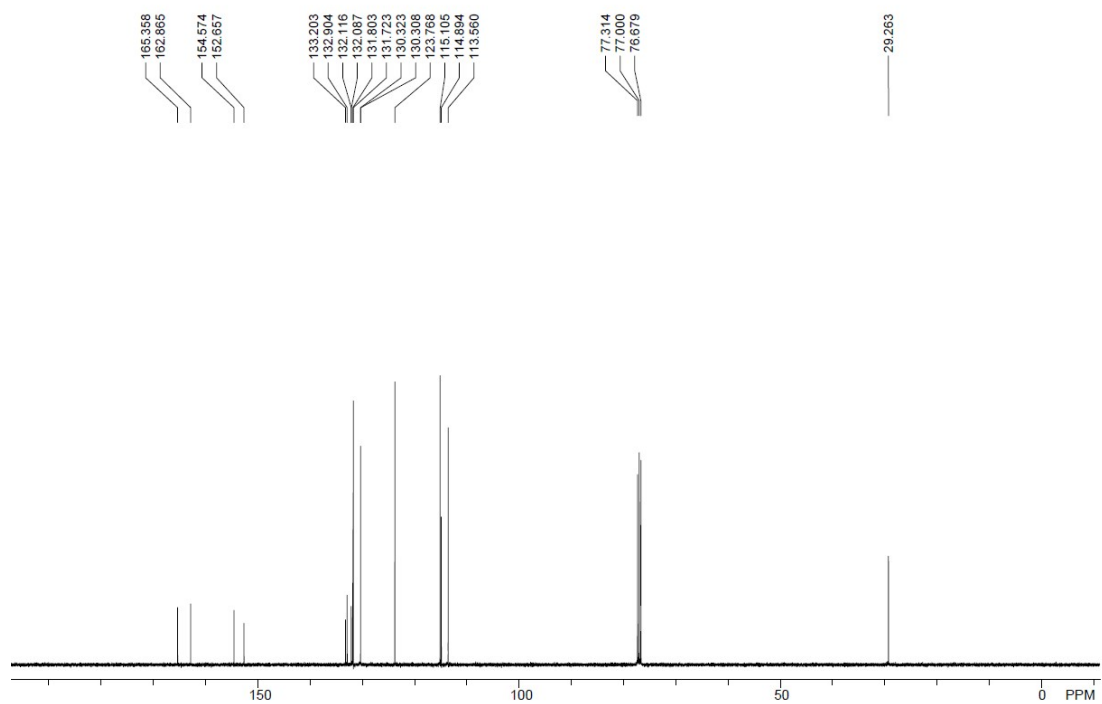


Figure S58. ^{13}C spectra of **3af**

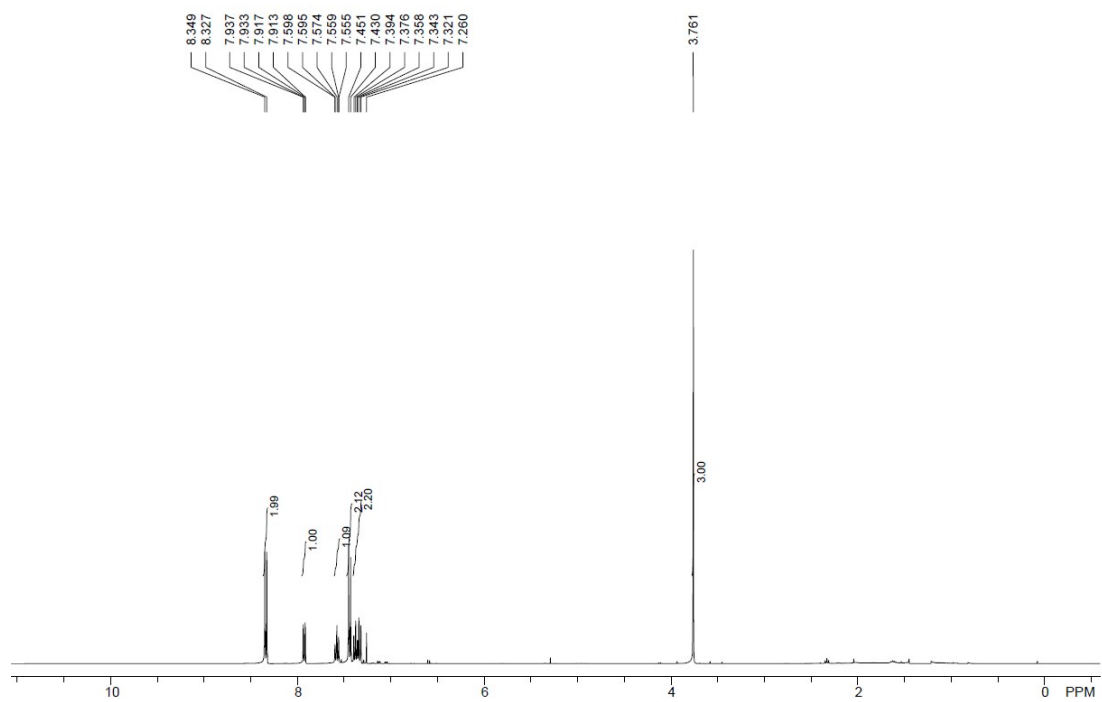


Figure S59. ^1H spectra of **3ag**

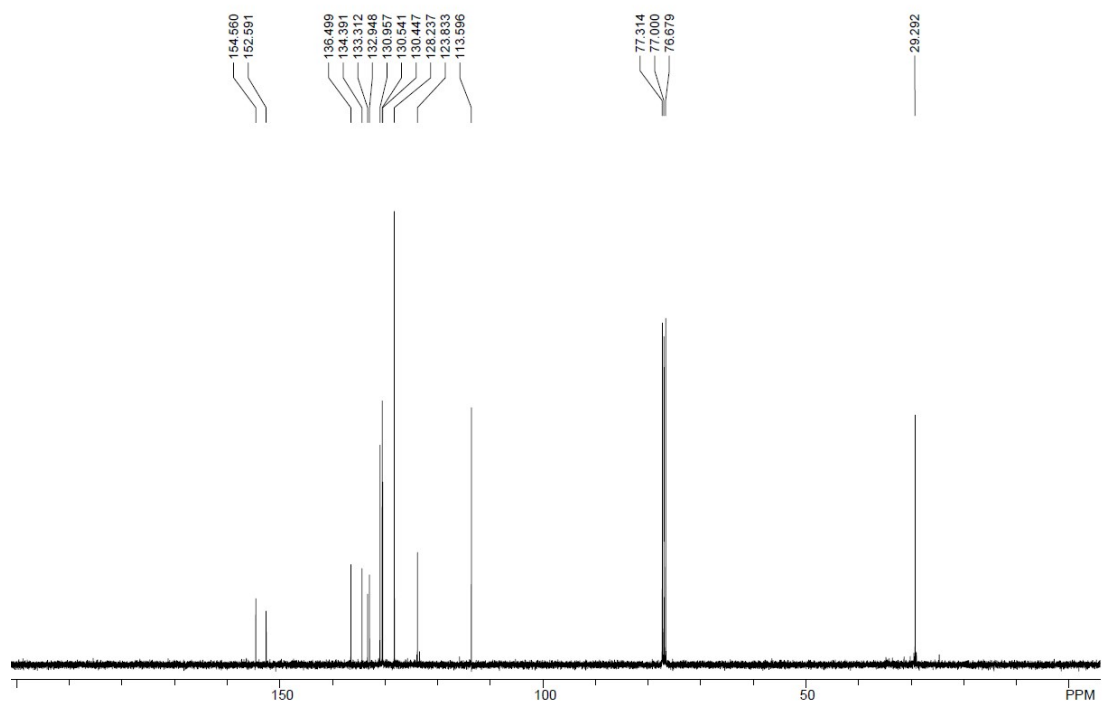


Figure S60. ^{13}C spectra of **3ag**

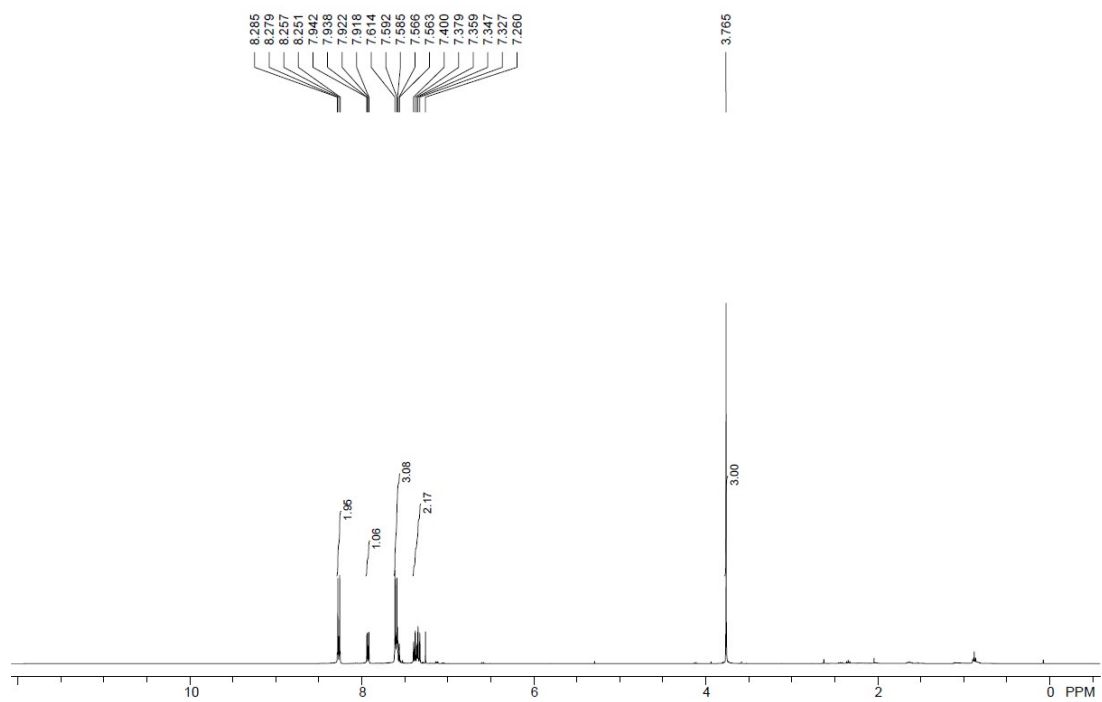


Figure S61. ^1H spectra of **3ah**

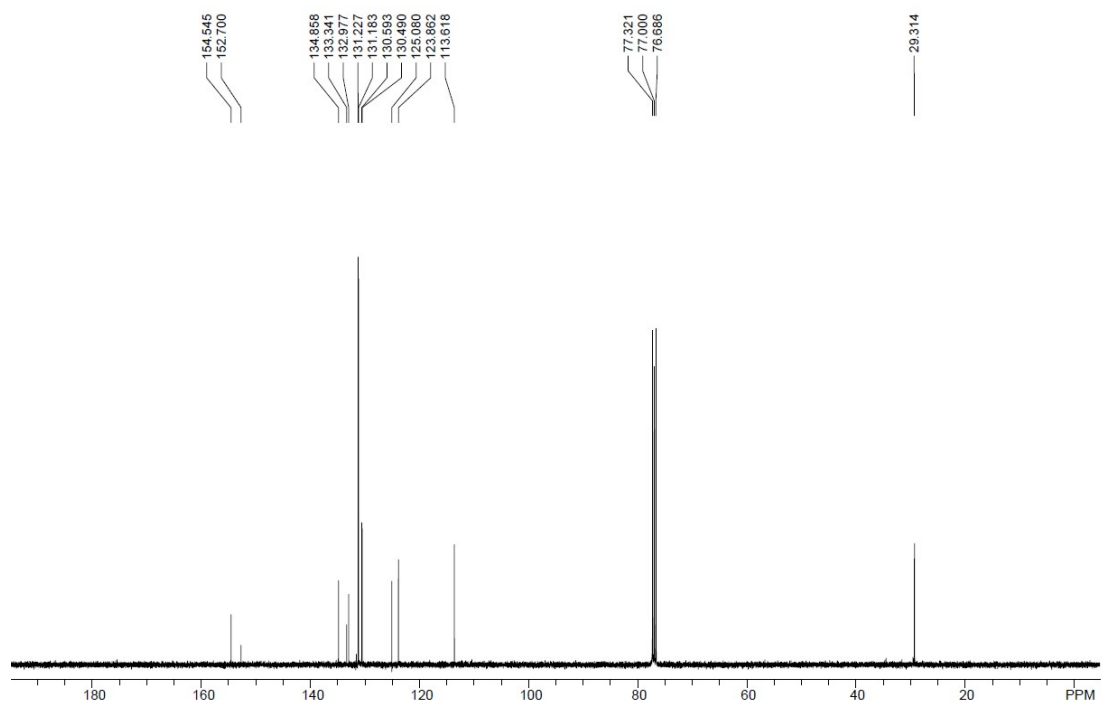


Figure S62. ^{13}C spectra of **3ah**

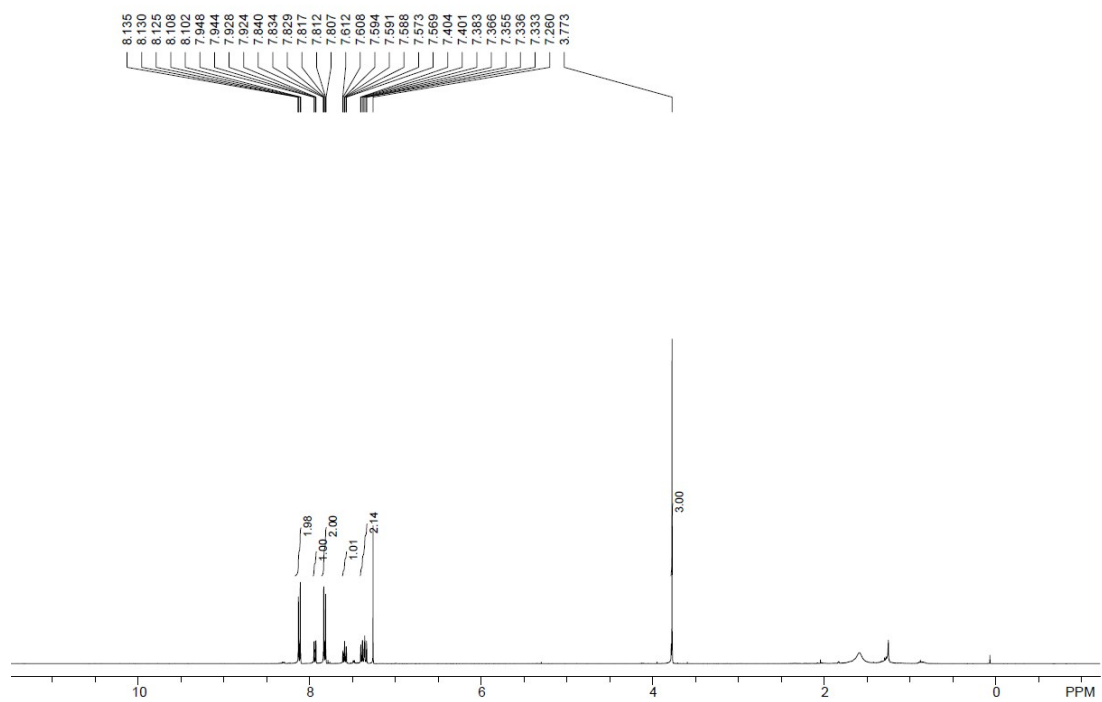


Figure S63. ^1H spectra of **3ai**

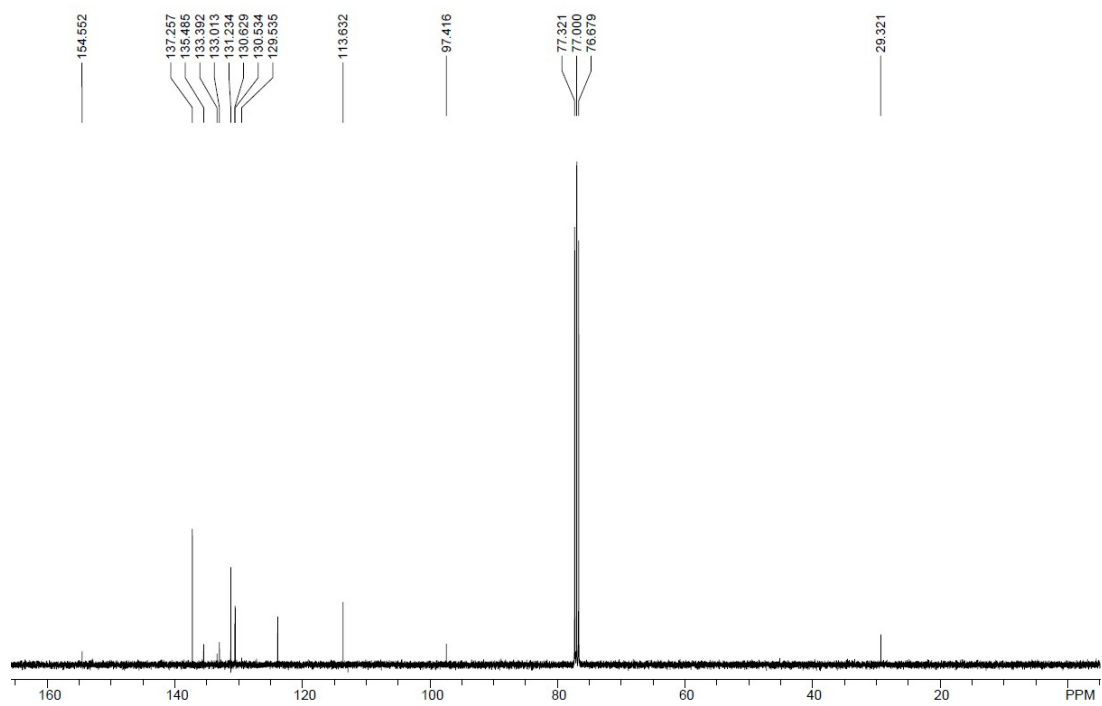


Figure S64. ^{13}C spectra of **3ai**

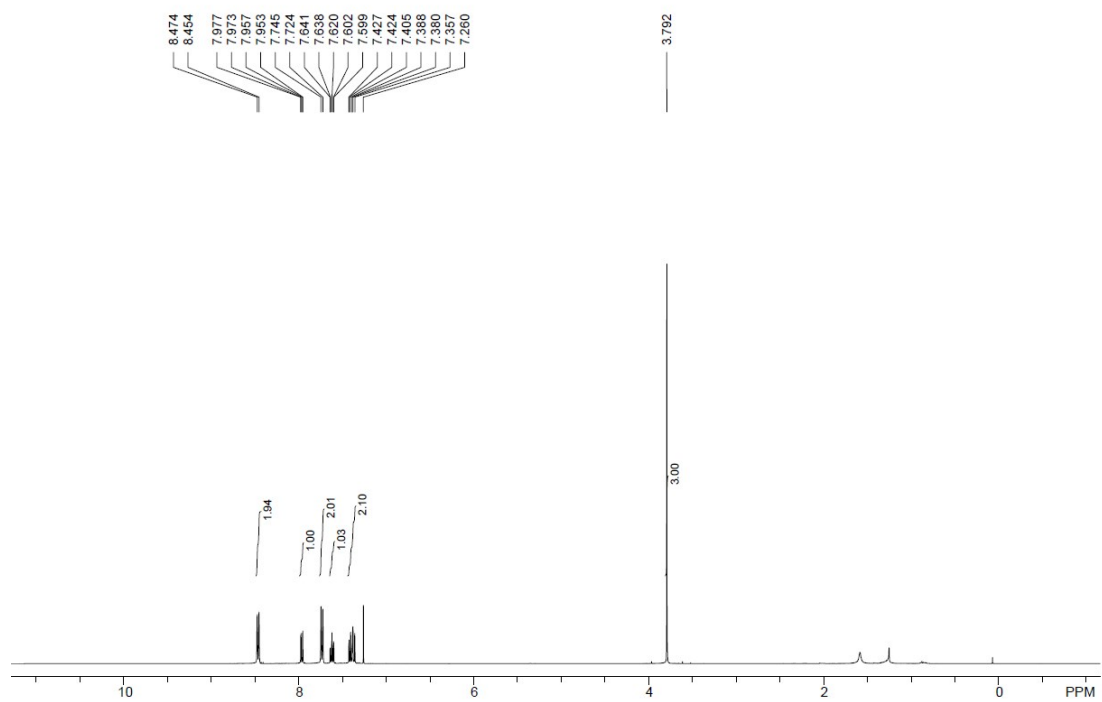


Figure S65. ^1H spectra of **3aj**

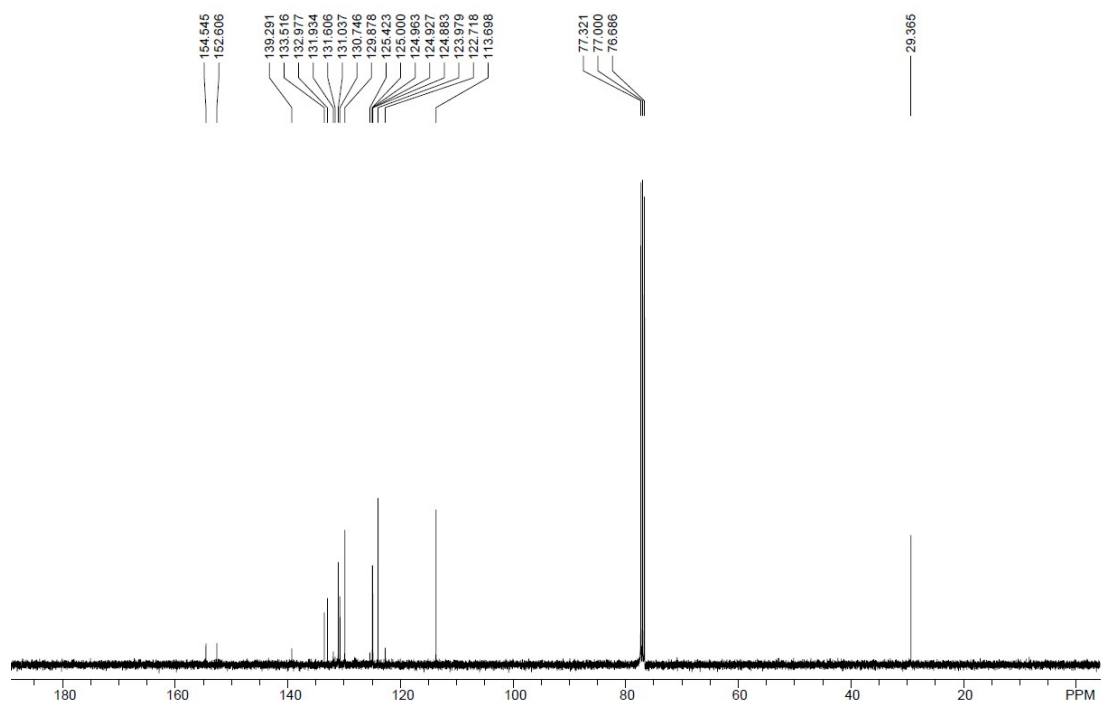


Figure S66. ^{13}C spectra of **3aj**

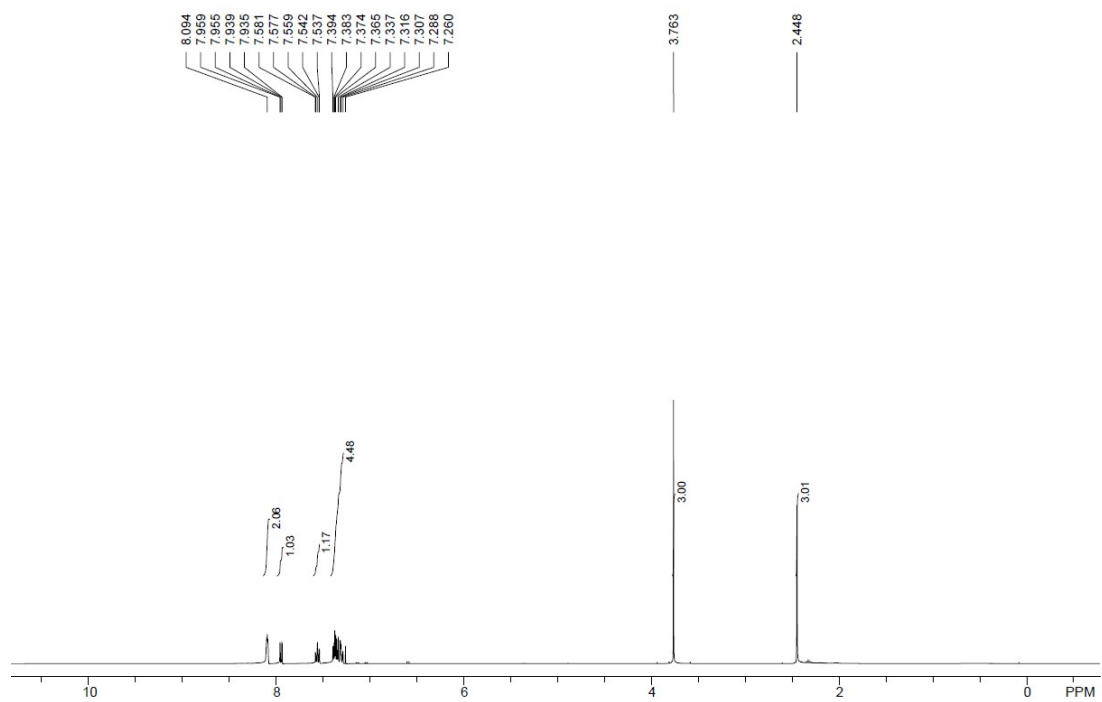


Figure S67. ^1H spectra of **3ak**

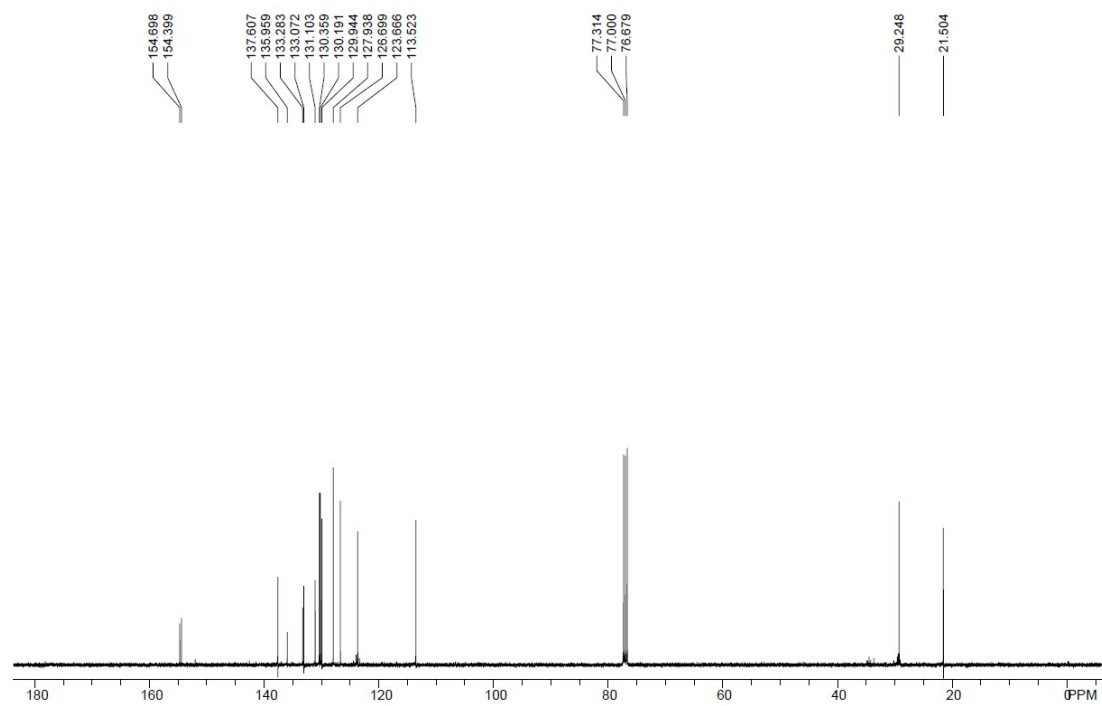


Figure S68. ^{13}C spectra of **3ak**

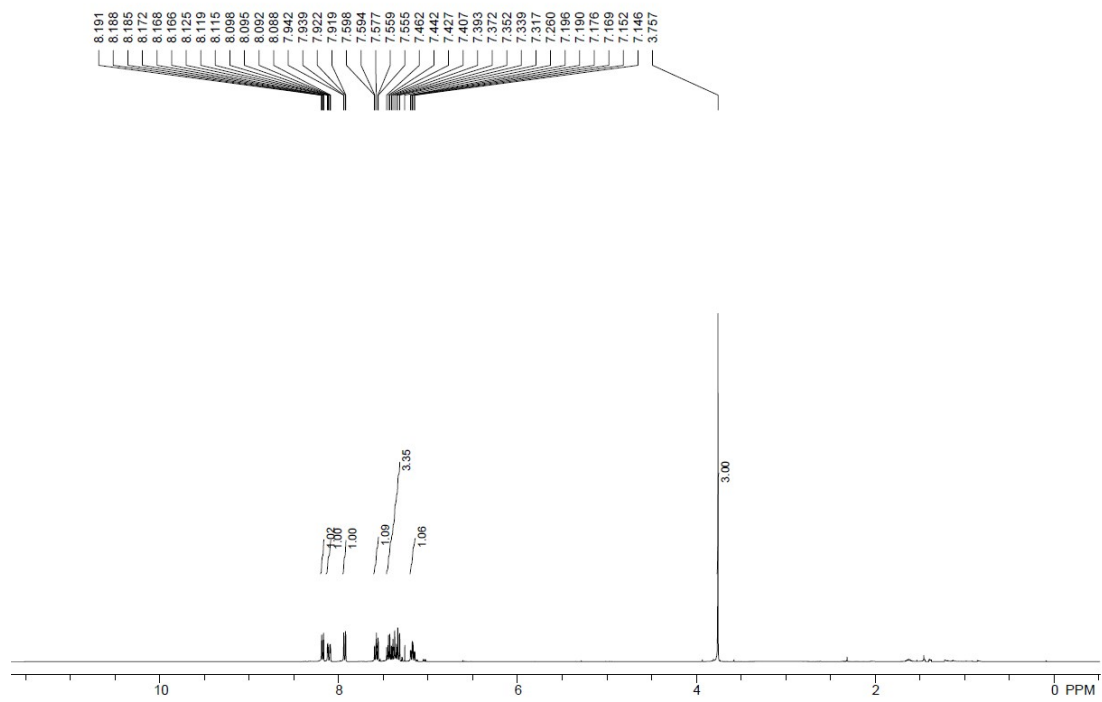


Figure S69. ¹H spectra of **3al**

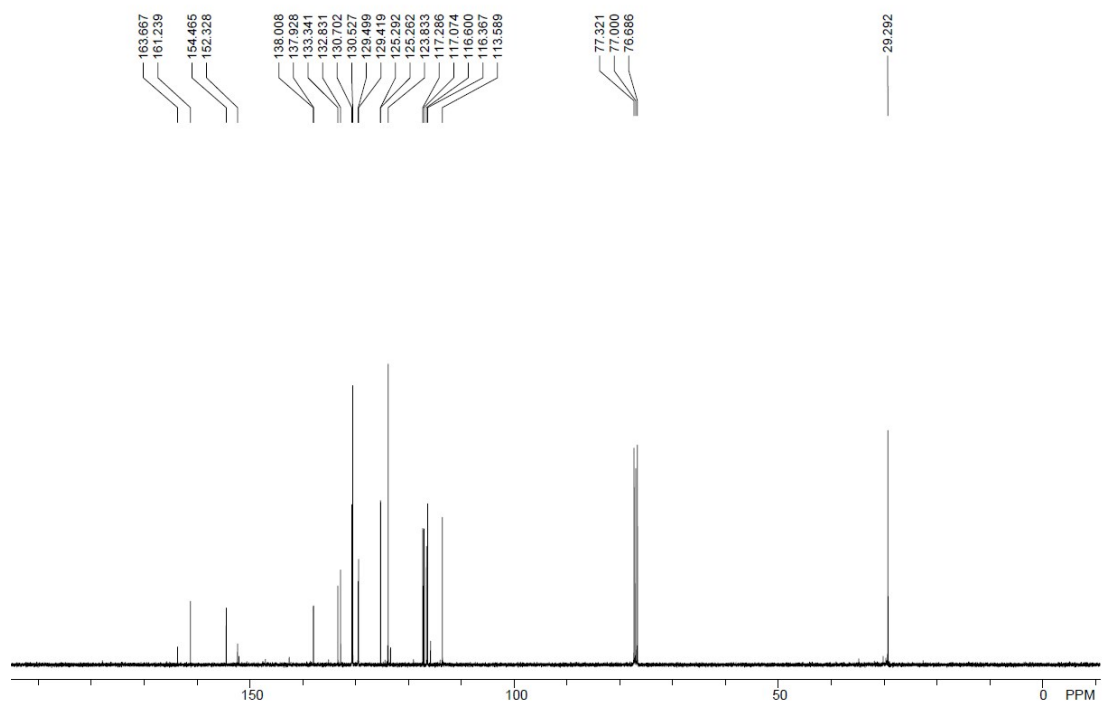


Figure S70. ¹³C spectra of **3al**

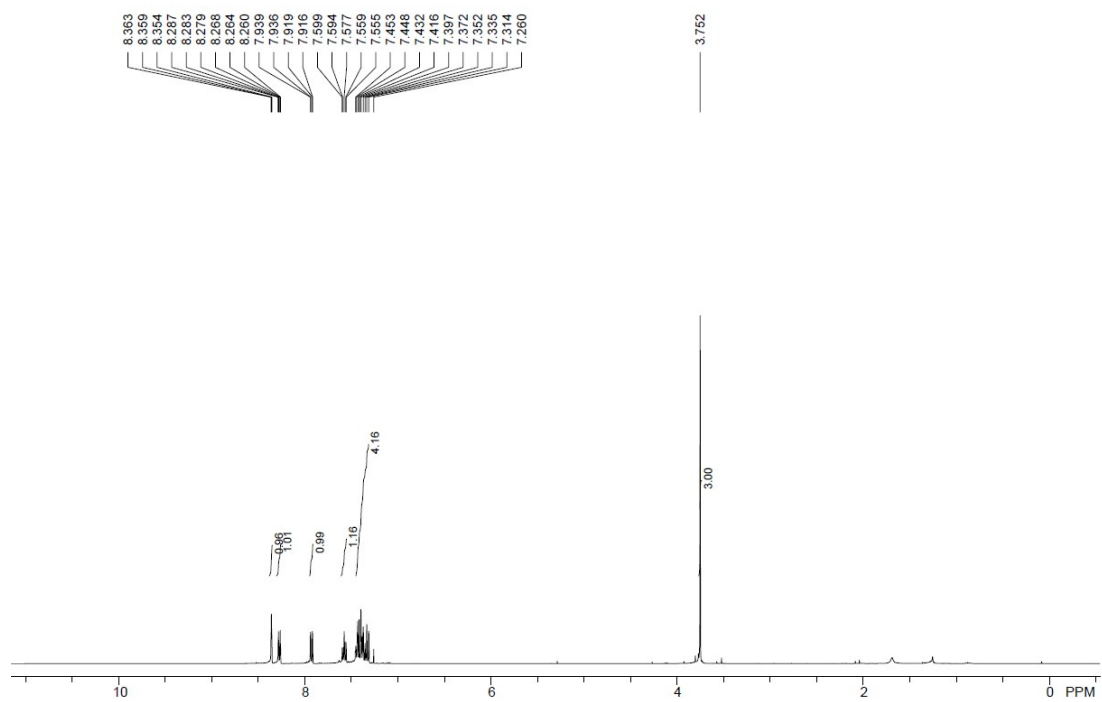


Figure S71. ^1H spectra of **3am**

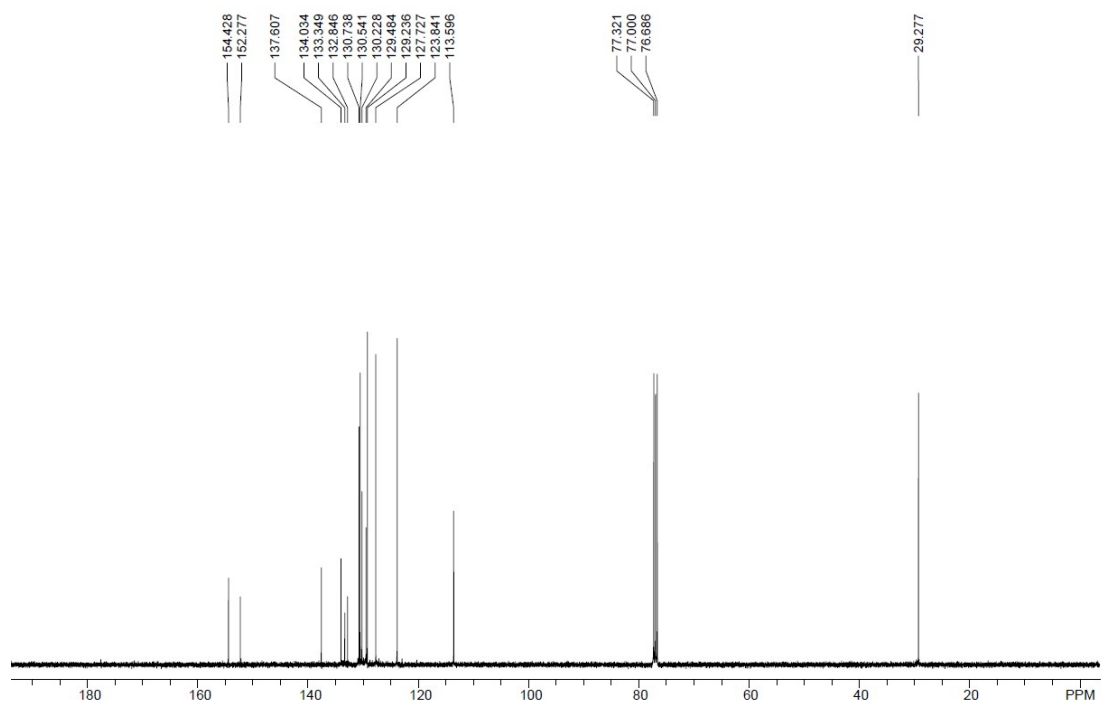


Figure S72. ^{13}C spectra of **3am**

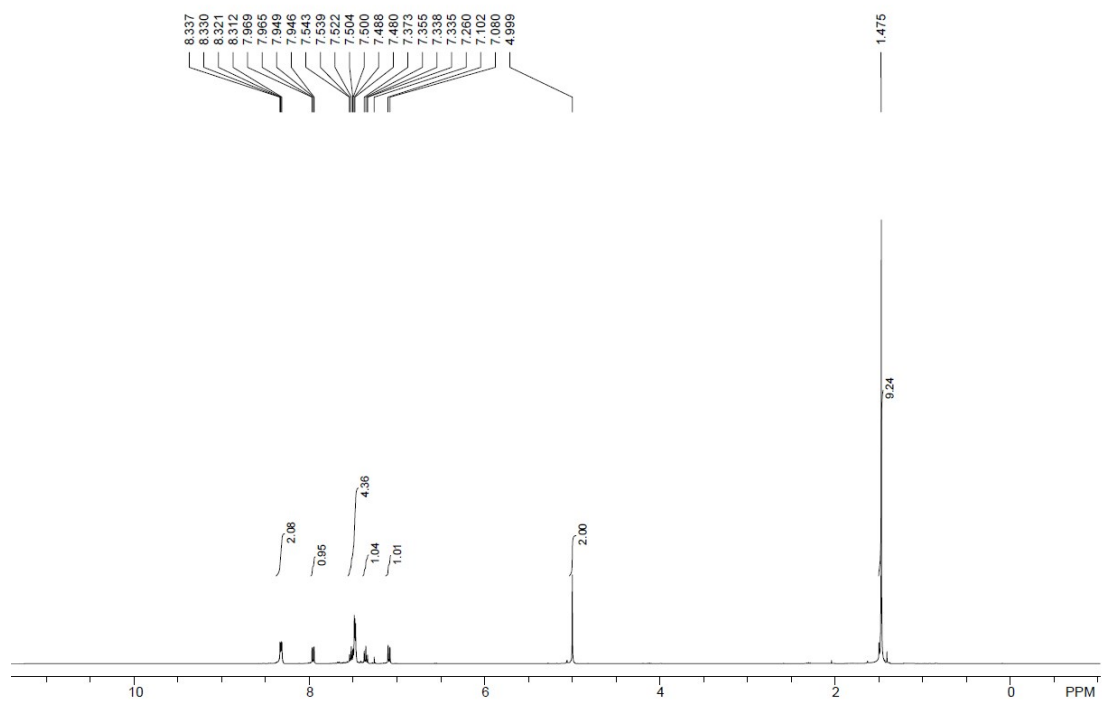


Figure S73. ^1H spectra of **3ua**

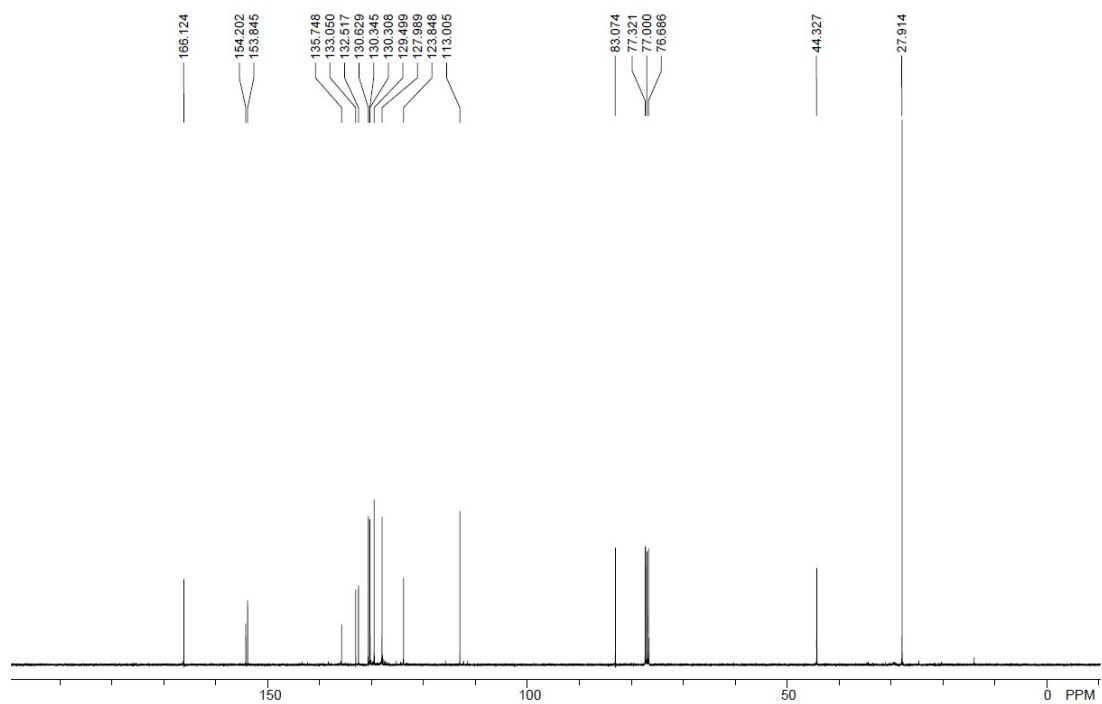


Figure S74. ^{13}C spectra of **3ua**