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Supplementary Information

Agarose-Alumina Composite Supported Palladium Catalyst for Suzuki Coupling Reactions

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General methods

NMR spectra were recorded on a Bruker-300 MHz spectrometer. Chemical shifts are reported relative to TMS; coupling constants are given in hertz. Melting points were measured on a WRS-2A meltingpoint apparatus and are uncorrected. Analytical TLC was performed on precoated silica gel 60 F254 plates. Yields refer to the isolated yields of the products after purification by silica-gel column chromatography (200-300 mesh). Commercial reagents were used as received. Analytical-grade solvents and commercially available reagents were used without further purification.

General procedure for the Suzuki coupling reaction

Aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), Pd@Al_2O_3-agarose (100 mg) and EtOH (5 mL) were added to a Schlenk flask. The mixture was stirred at room temperature under air. Upon complete consumption of starting materials, as determined by TLC analysis, the solid was filtered and washed with acetone (3 × 5 mL). The combined organic solvents were concentrated in vacuum to afford product which was purified by silica gel column chromatography (petroleum ether/EtOAc = 10:1).

4-Methyl-1,1'-biphenyl (**6a**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 7.23 (m, 2H), 7.31 (d, 1H, *J* 7.2 Hz), 7.41 (m, 2H), 7.48 (d, 2H, *J* 7.9 Hz), 7.57 (d, *J* 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 126.9, 127.0, 128.7, 129.5, 136.9, 138.4, 141.2.

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Methyl 2-methyl-[1,1'-biphenyl]-3-carboxylate (**6b**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.90 (s, 3H), 7.28 (m, 3H), 7.40 (m, 4H), 7.80 (d, 1H, *J* 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.4, 20.6, 29.7, 51.9, 52.2, 125.2, 126.7, 127.1, 128.1, 129.1, 129.3, 131.4, 133.2, 135.8, 136.6, 168.8.

2-Methyl-1,1'-biphenyl (**6c**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.27 (s, 3H), 7.25 (m, 4H), 7.33 (m, 3H), 7.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.4, 125.7, 126.7, 127.1, 127.2, 128.0, 128.7, 129.2, 129.8, 130.3, 135.3, 141.9.

1,1'-Biphenyl (**6d**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (m, 2H), 7.44 (m, 4H), 7.66 (d, 4H, *J* 8.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 127.1, 127.4, 128.5, 140.2.

2-Methoxy-1,1'-biphenyl (**6e**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 3H), 7.01 (d, 2H, *J* 8.0 Hz), 7.33 (m, 3H), 7.40 (t, 2H, *J* 7.4 Hz), 7.53 (d, 2H, *J* 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.3, 121.8, 125.6, 127.9, 128.6, 128.7, 128.9, 129.3, 136.6, 157.9.

4-Methoxy-1,1'-biphenyl (**6f**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.97 (d, 2H, *J* 8.6 Hz), 7.29 (m, 2H), 7.43 (m, 2H), 7.53 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 114.2, 126.6, 126.7, 128.1, 128.7, 133.8, 140.8, 141.8, 159.2.

1-Phenylnaphthalene (**6g**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (m, 9H), 7.88 (dd, 3H, *J* 12.8, 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.6, 126.1, 126.3, 127.4, 127.6, 127.9, 128.4, 130.3, 131.9, 134.2, 140.5, 141.1.

2,6-Dimethyl-1,1'-biphenyl (**6h**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.03 (s, 6H), 7.13 (m, 4H), 7.33 (m, 1H), 7.41 (m, 2H), 7.59 (d, 1H, *J* 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.8, 125.1, 126.6, 126.9, 127.1, 127.2, 127.3, 128.4, 128.7, 129.0, 136.0, 141.1, 141.9.

[1,1'-Biphenyl]-4-yl(phenyl)methanone (**6i**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (m, 1H), 7.49 (m, 4H), 7.58 (d, 1H, *J* 7.4 Hz), 7.63 (d, 2H, *J* 7.0 Hz), 7.70 (d, 2H, *J* 8.5 Hz), 7.83 (d, 2H, *J* 7.0 Hz), 7.89 (d, 2H, *J* 8.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 126.9, 127.3, 128.2, 128.3, 128.9, 129.9, 130.7, 132.3, 136.3, 137.8, 139.9, 145.2, 196.3.

1-([1,1'-Biphenyl]-4-yl)ethanone (**6j**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.62 (s, 3H), 7.44 (m, 3H), 7.62 (d, 2H, *J* 7.6 Hz), 7.67 (d, 2H, *J* 8.3 Hz), 8.02 (d, 2H, *J* 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.6, 127.1, 127.2, 128.2, 128.8, 128.9, 135.8, 139.8, 145.7, 197.6.

4-Nitro-1,1'-biphenyl (**6k**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 3H), 7.61 (d, 2H, *J* 7.7 Hz), 7.72 (d, 2H, *J* 8.7 Hz), 8.27 (d, 2H, *J* 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 124.0, 127.3, 127.7, 128.9, 129.1, 138.9, 147.2, 147.7.

4-(Trifluoromethoxy)-1,1'-biphenyl (**6l**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, 2H, *J* 8.2 Hz), 7.41 (t, 1H, *J* 7.3 Hz), 7.51 (m, 2H), 7.62 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 118.7, 121.2, 122.4, 127.1, 127.7, 128.5, 128.9, 139.8, 139.9, 148.5.

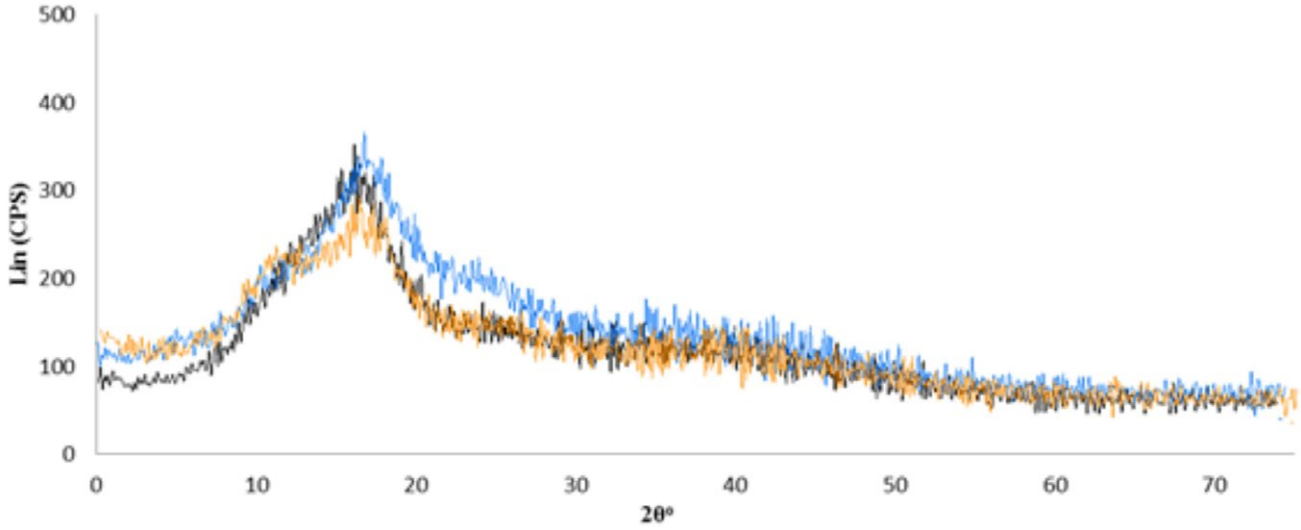

Figure S1. XRD patterns of agarose (black), Al_2O_3-agarose (blue) and Pd@Al_2O_3-agarose catalyst (orange).

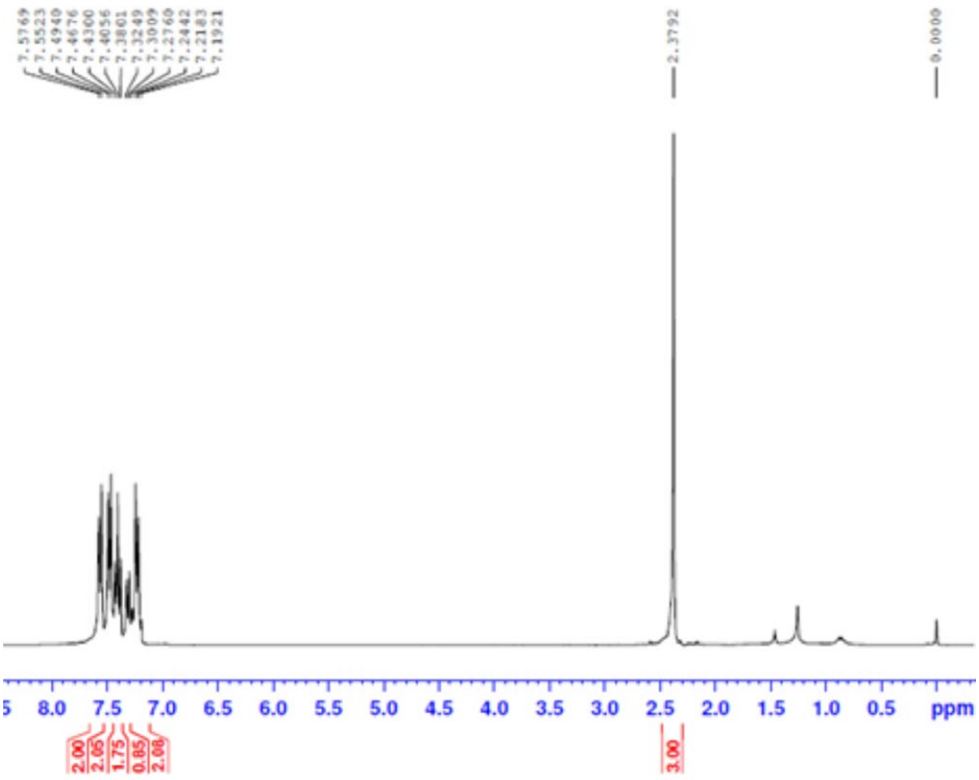

Figure S2. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **6a**.

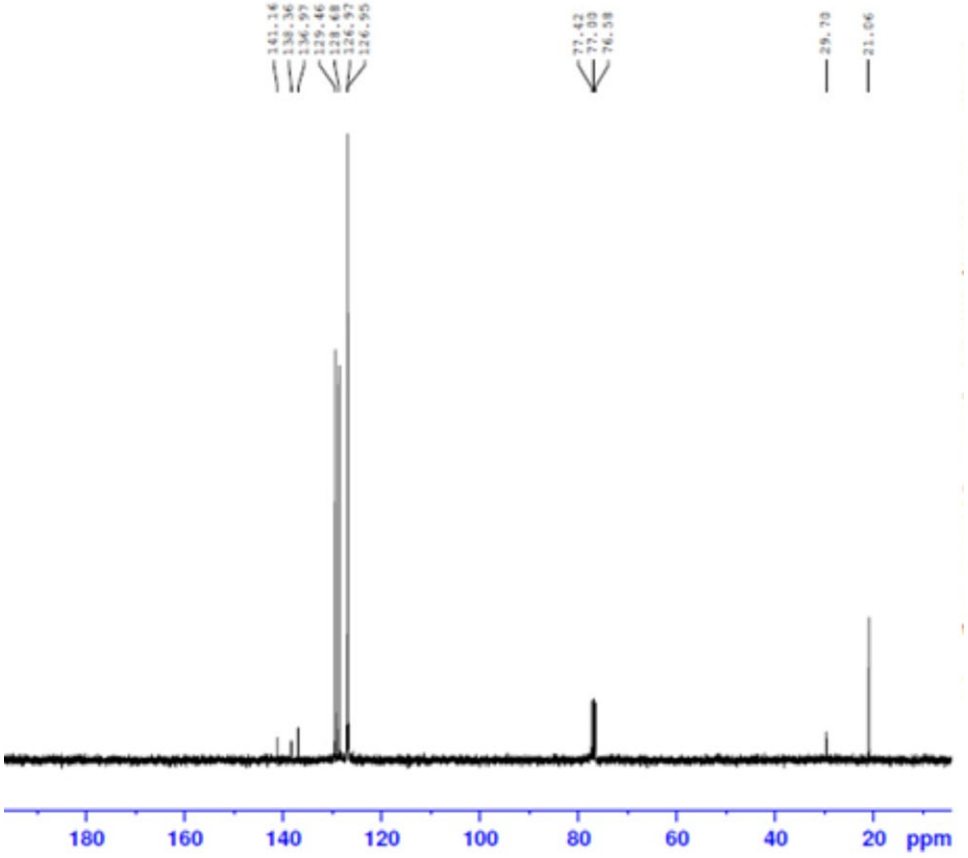

Figure S3. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **6a**.

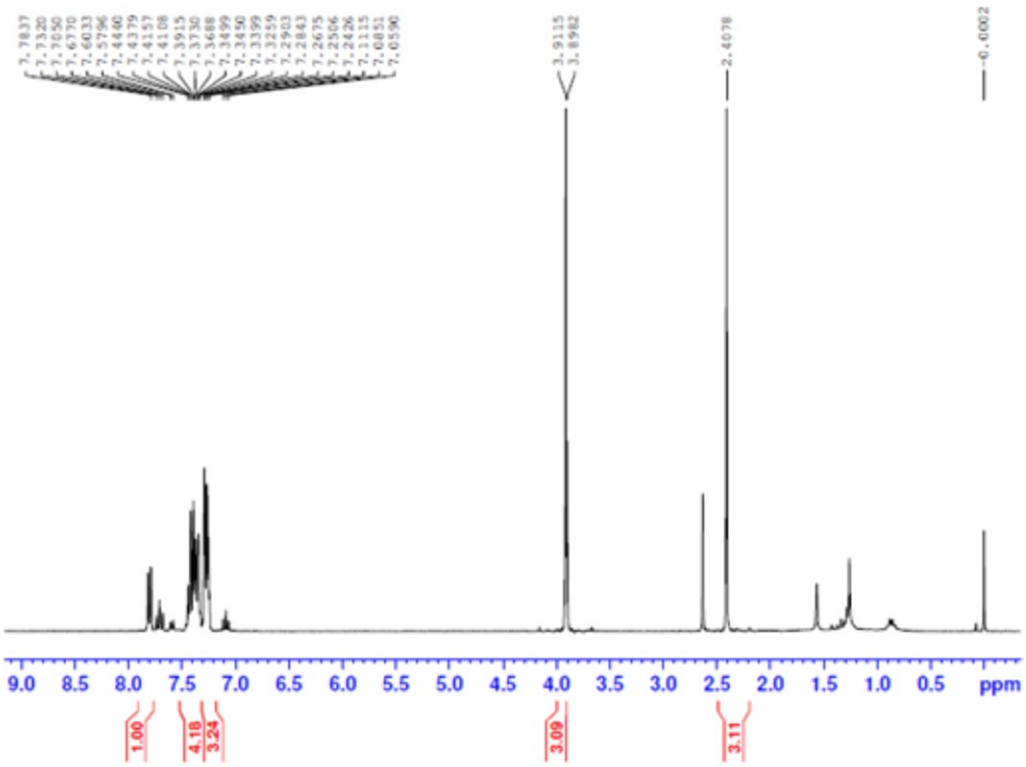

Figure S4. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **6b**.

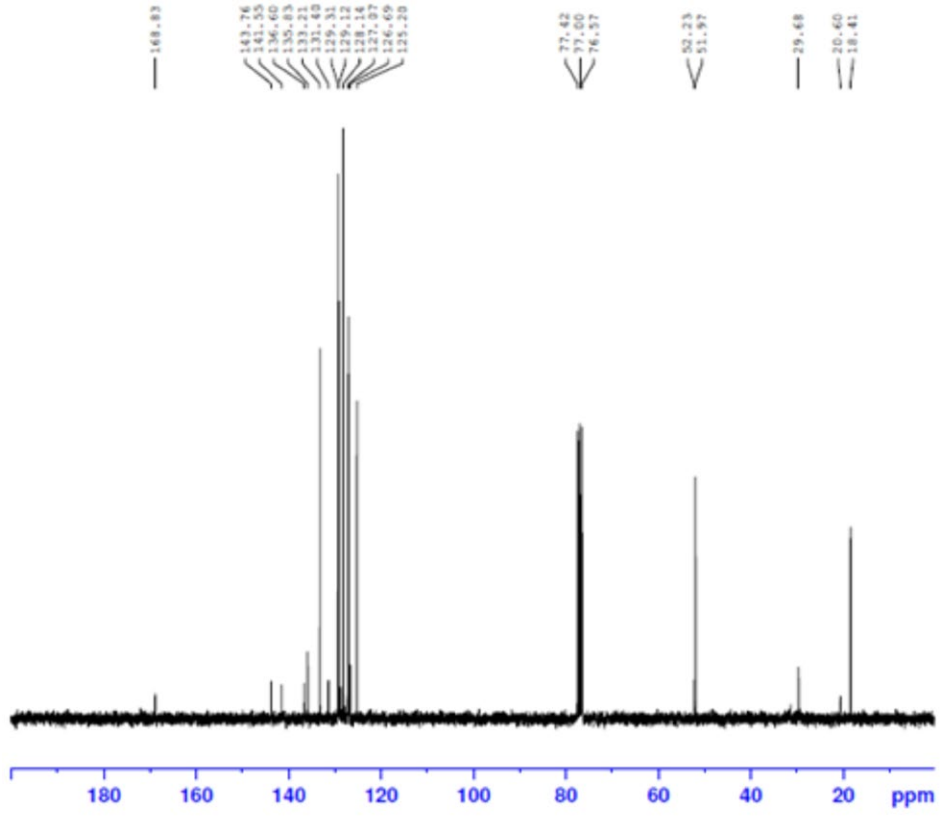

Figure S5. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **6b**.

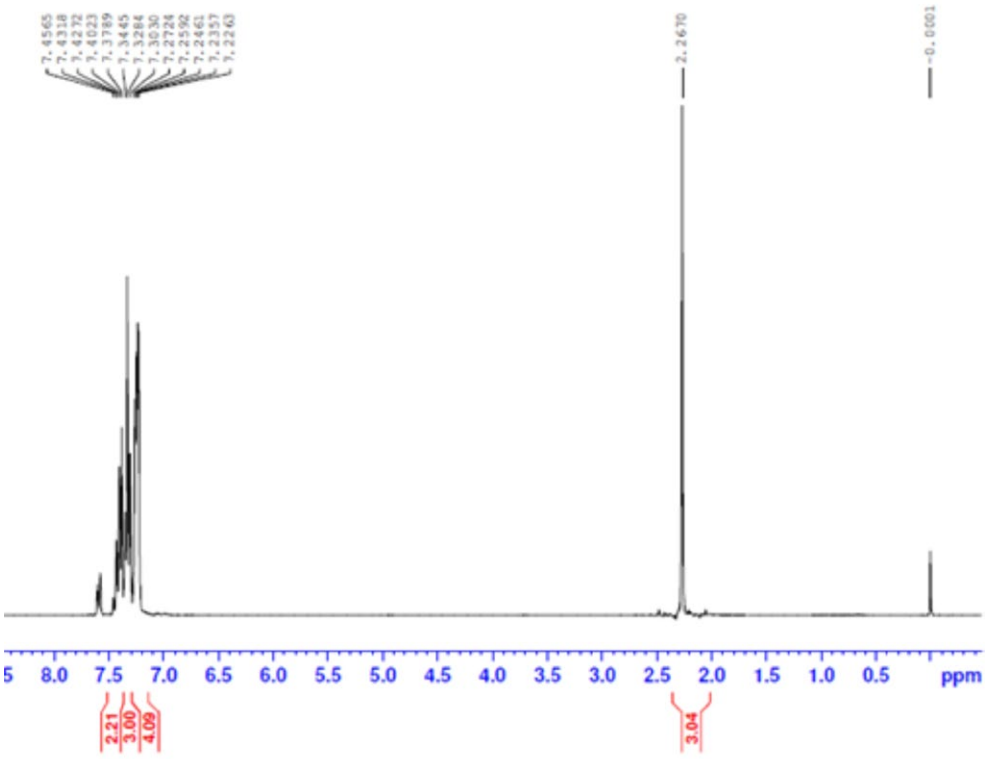

Figure S6. [1]H NMR (300 MHz, $CDCl_3$) spectrum of compound **6c**.

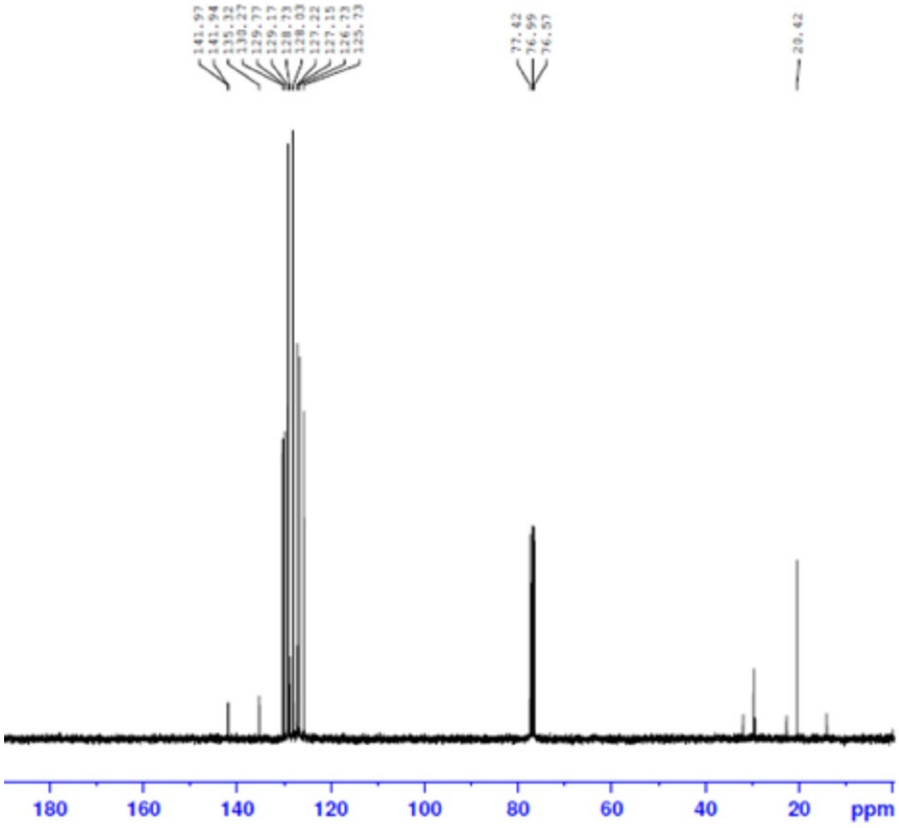

Figure S7. [13]C NMR (75 MHz, $CDCl_3$) spectrum of compound **6c**.

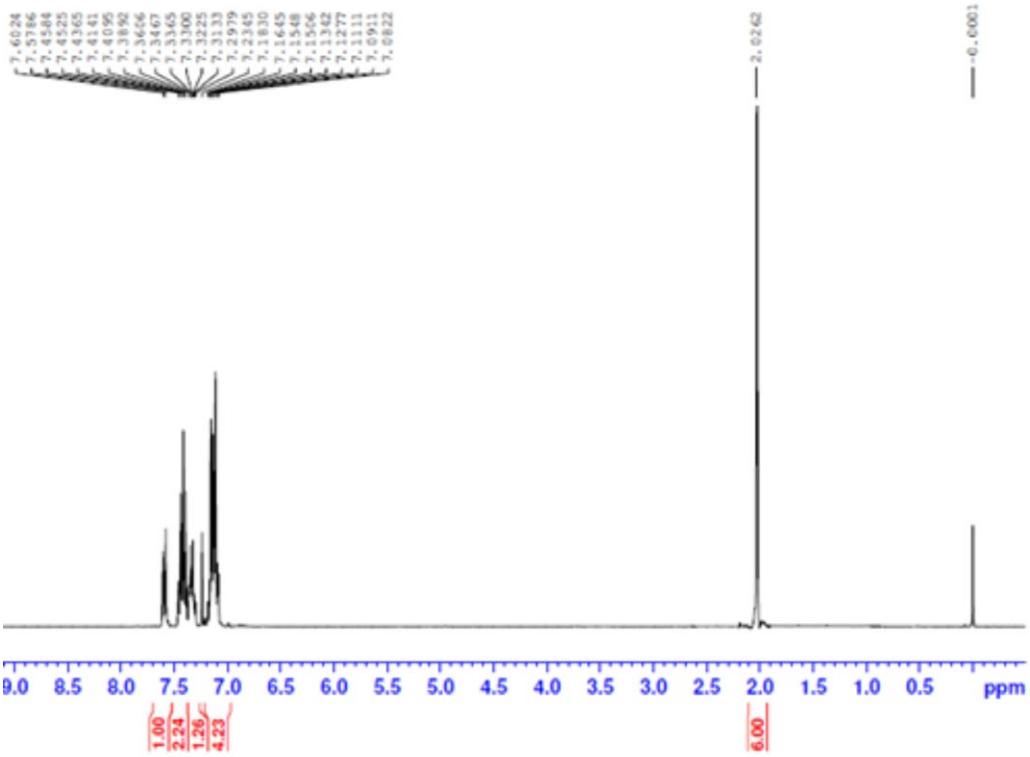

Figure S8. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **6h**.

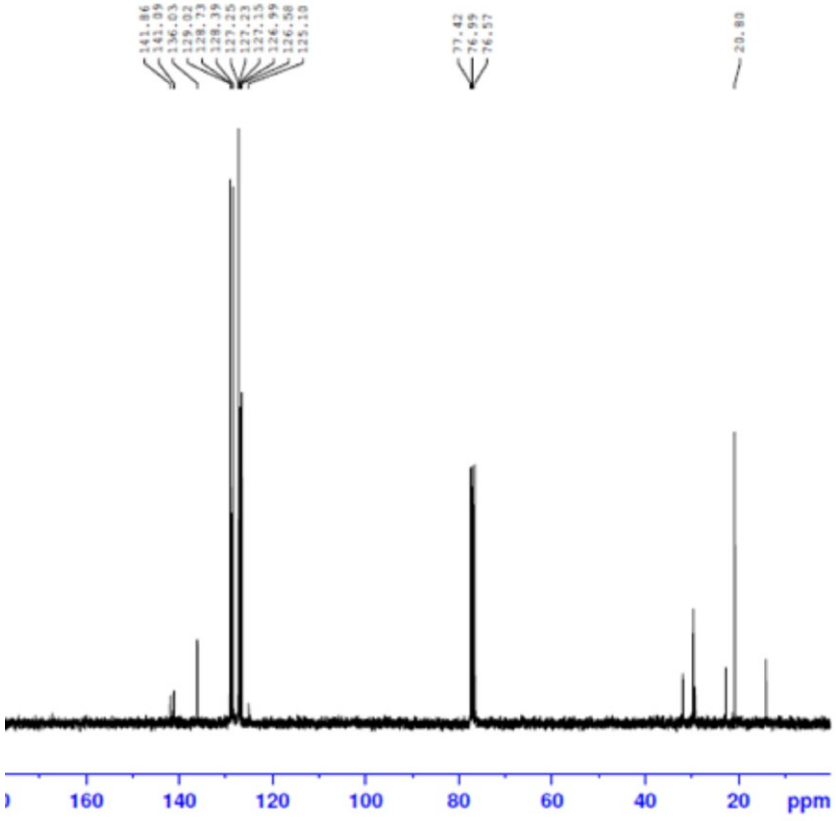

Figure S9. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **6h**.

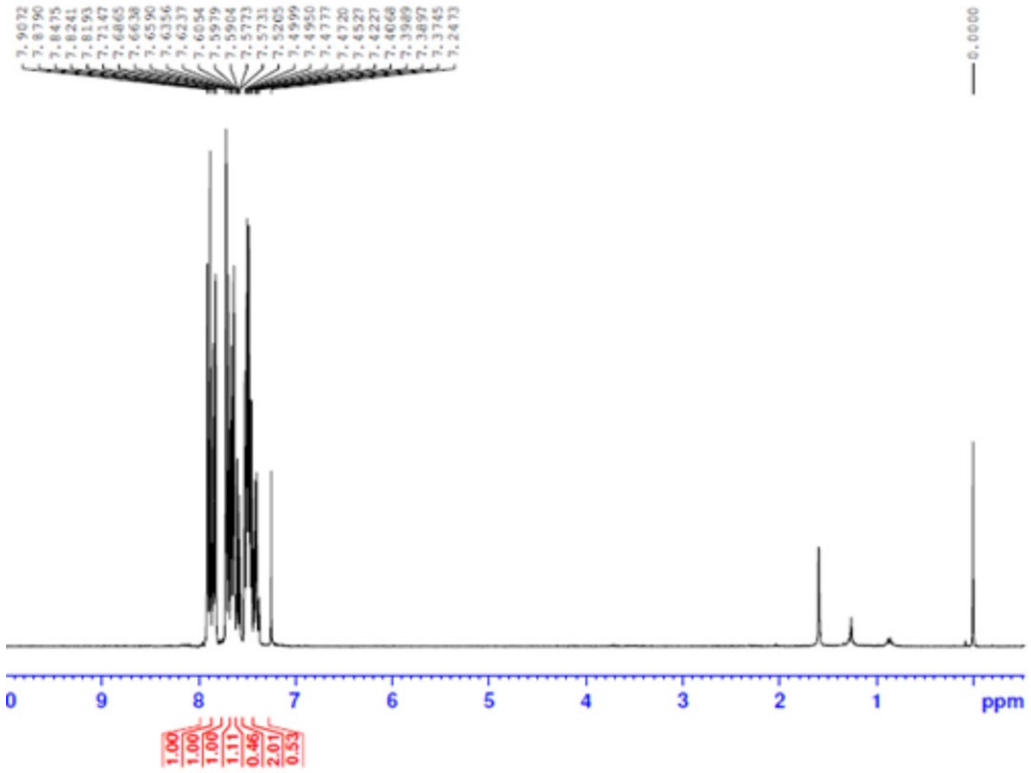

Figure S10. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **6i**.

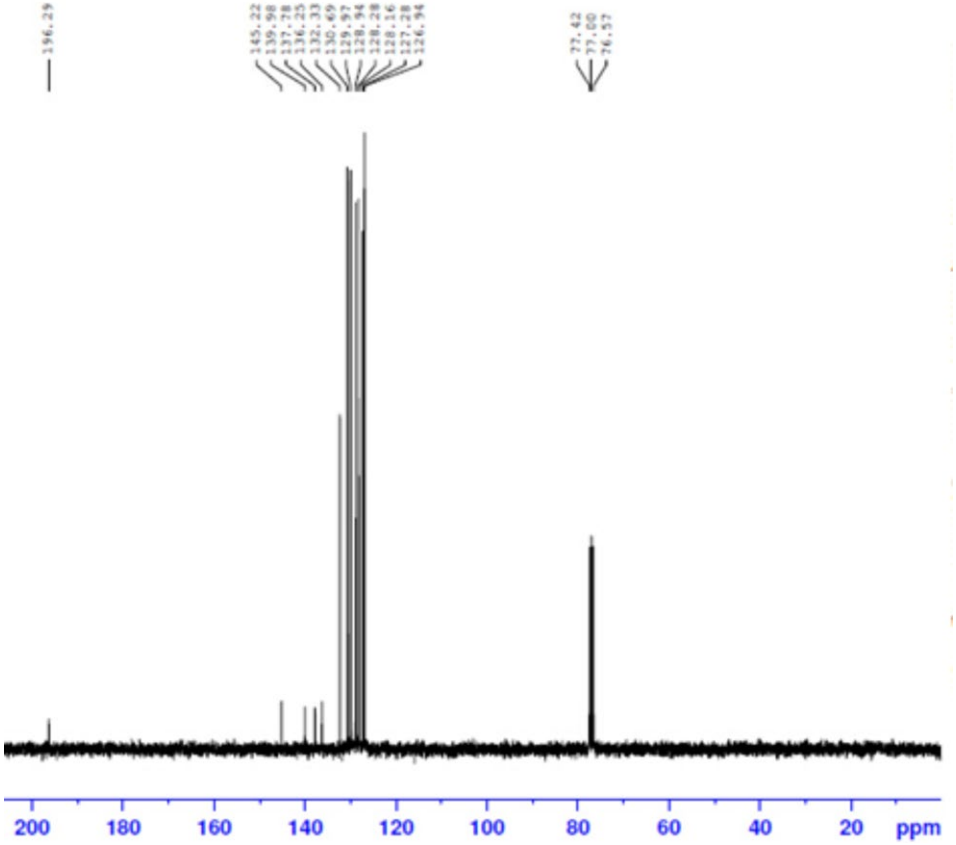

Figure S11. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **6i**.

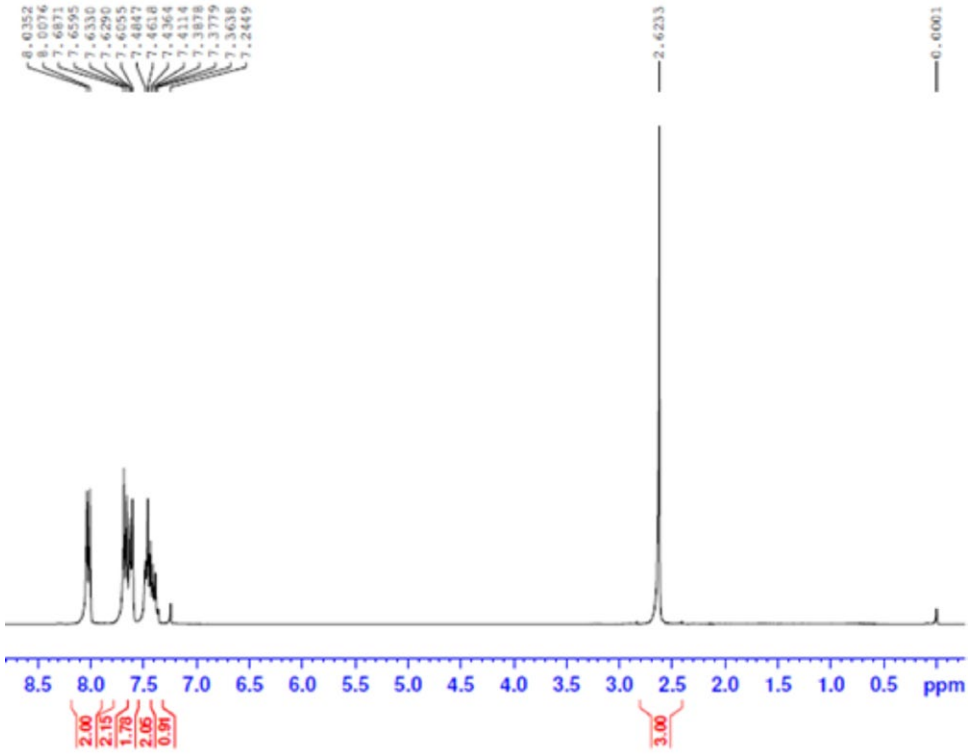

Figure S12. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **6j**.

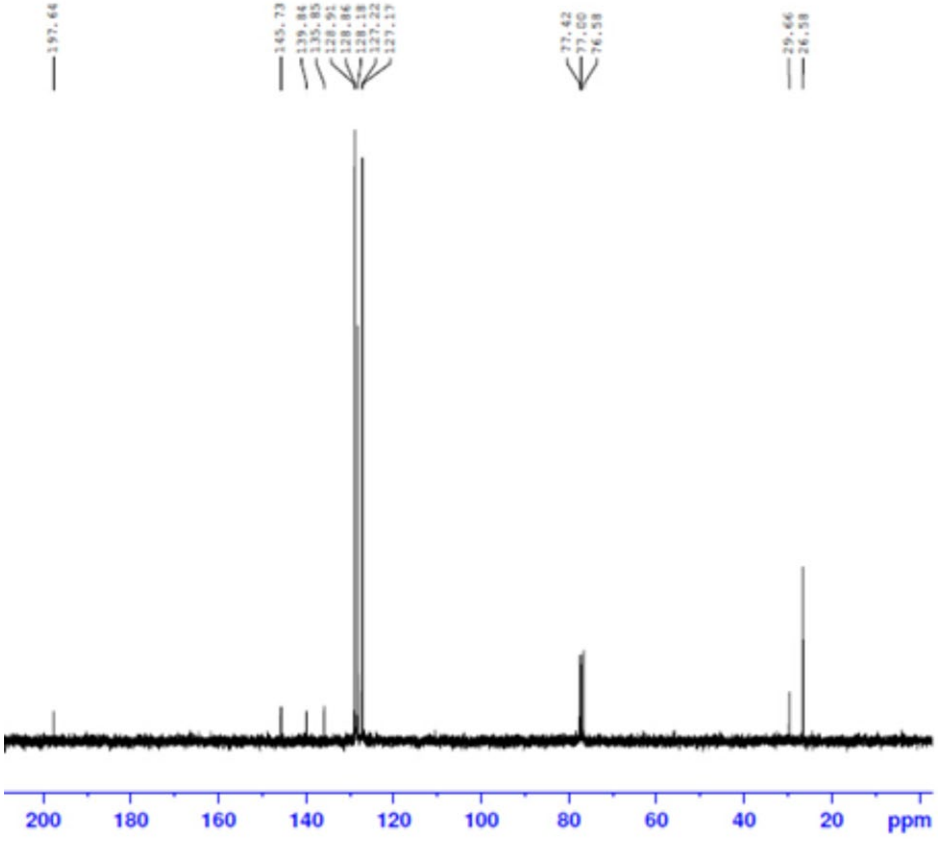

Figure S13. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **6j**.

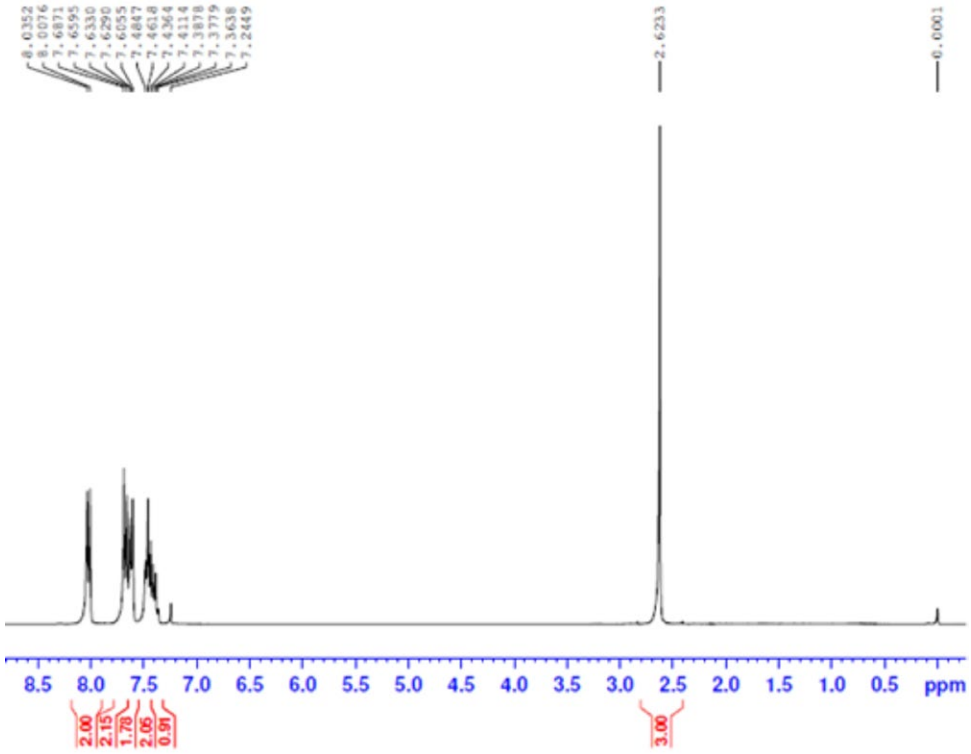

Figure S14. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **6k**.