Supporting Information

Visible-light-promoted tandem radical difunctionalization of olefinic amides: A direct access to NO_2-containing benzoxazines and oxazolines

Renu Chaudhary[a]*

[a]Department of Chemistry, Mehr Chand Mahajan DAV College for Women, Chandigarh-160036, India

renu@mcmdavcwchd.in

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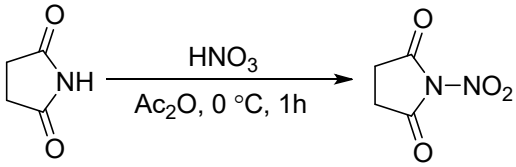
General Information

All the reagents and substrates were purchased from commercial suppliers with best quality and were used without further purification. All the solvents were distilled prior use according to the established procedures.[1] The column chromatography was carried out using silica gel with 100-200 mesh size. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ with TMS as an internal standard. Chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz). Data of the peaks are reported as follows: s, singlet; d, doublet, t, triplet; m, multiplet; dd, doublet of doublet; and so on. High-resolution mass spectra (HRMS) were collected by ESI-Q-TOF Premier mass spectrometer. Visible light irradiation was carried out using high-power blue LEDs Philips LUXEON® Rebel (9 W, λ = 455±5 nm). *N*-allylamides (**4**) were prepared according to the literature procedures.[2]

Synthesis of *N*-Nitrosuccinimide (2): This compound was prepared according to the previously reported procedure.[3]



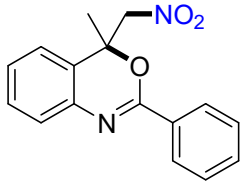
***N*-Nitrosuccinimide (2)**: White solid, m.p. 88 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.92 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168, 27.12. HRMS (ESI), calcd for $C_4H_4N_2O_4$ [M]+ 144.0171, found144.0170.

General experimental details

A 20-mL vial equipped with magnetic stir bar was charged with olefinic amides (0.5 mmol, 1.0 equiv.), *N*-Nitrosuccinimides (1.0 mmol, 2.0 equiv.) and $Ru(bpy)_3(PF_6)_2$ (3 mol%) and the mixture was degassed by "pump-freeze-thaw" cycles (x3) via a syringe needle. Then dry CH_3CN (3.0 mL) was injected under Ar and the resulting mixture was stirred at room temperature under 9 W blue LEDs for 7 h. After completion of the reaction (as indicated by TLC), the mixture was diluted by adding ethyl acetate and brine. The aqueous layer was extracted with ethyl acetate (x3) and combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The crude products were further purified by filtration through short-pad of silica-gel column

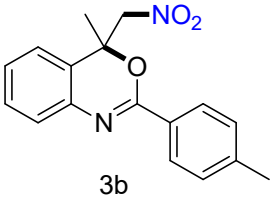
chromatography using mixture of ethyl acetate and *n*-hexane. The identity and purity of the products was confirmed by spectroscopic analysis.

Experimental characterization data for products



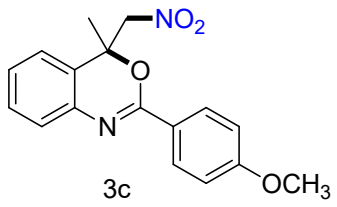
3a

4-methyl-4-(nitromethyl)-2-phenyl-4H-benzo[d][1,3]oxazine (3a): Yellow solid 81% (81 mg) , m.p. 75-77 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (dt, *J* = 6.9, 1.2 Hz, 2H), 7.56 – 7.46 (m, 3H), 7.45 – 7.38 (m, 1H), 7.32 – 7.24 (m, 3H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.53, 141.34, 135.89, 132.49, 131.15, 129.12, 127.27, 125.11, 124.73, 84.41, 25.41. HRMS (ESI), calcd for $C_{16}H_{14}N_2O_3$ $[M+H]^+$ 283.1038, found 283.1039.



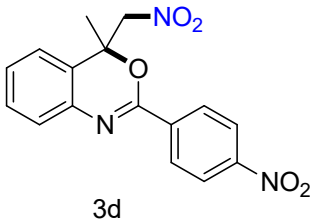
3b

4-methyl-4-(nitromethyl)-2-(p-tolyl)-4H-benzo[d][1,3]oxazine (3b): Yellow oil 84% (78 mg) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 2H), 7.47 – 7.38 (m, 1H), 7.34 – 7.26 (m, 2H), 7.30 – 7.20 (m, 3H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 2.26 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.53, 141.89, 141.34, 135.89, 131.29, 129.39, 129.14, 128.12, 125.21, 125.00, 124.73, 84.40, 25.41, 21.42. HRMS (ESI), calcd for $C_{17}H_{16}N_2O_3$ $[M+H]^+$ 297.1194, found 297.1195.



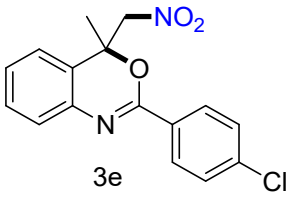
3c

2-(4-methoxyphenyl)-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3c): Yellow oil 89% (81 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 2H), 7.46 – 7.38 (m, 1H), 7.33 – 7.21 (m, 3H), 6.94 – 6.86 (m, 2H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 3.82 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.00, 162.56, 141.36, 135.91, 132.24, 129.94, 129.17, 125.13, 124.76, 114.53, 84.43, 55.38, 25.43. HRMS (ESI), calcd for $C_{17}H_{16}N_2O_4$ $[M+H]^+$ 313.1144, found 313.1145.



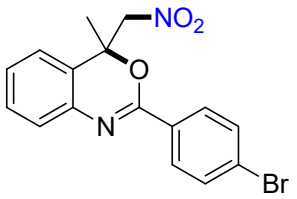
3d

4-methyl-4-(nitromethyl)-2-(4-nitrophenyl)-4H-benzo[d][1,3]oxazine (3d): Pale yellow solid 74% (71 mg), m.p. 80-82 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 – 8.20 (m, 2H), 8.11 – 8.03 (m, 2H), 7.47 – 7.38 (m, 1H), 7.34 – 7.21 (m, 3H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.53, 148.49, 141.34, 135.89, 134.64, 131.26, 129.14, 125.11, 124.73, 124.01, 84.41, 25.41. HRMS (ESI), calcd for $C_{16}H_{13}N_3O_5$ $[M+H]^+$ 328.0889, found 328.0888.



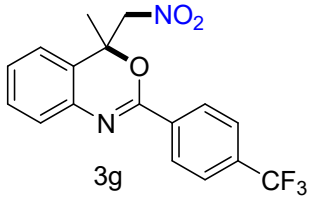
3e

2-(4-chlorophenyl)-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3e): White solid 72% (85 mg), m.p. 118-120 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.44 – 7.41 (m, 1H), 7.39 – 7.35 (m, 2H), 7.32 – 7.22 (m, 3H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.53, 141.34, 136.70, 135.89, 133.23, 131.41, 129.51, 129.14, 125.21, 125.00, 124.14, 84.41, 25.41. HRMS (ESI), calcd for $C_{16}H_{13}ClN_2O_3$ $[M+H]^+$ 318.0585, found 318.0584.



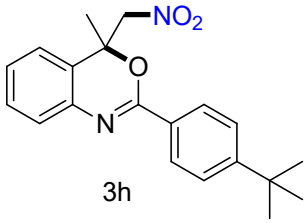
3f

2-(4-bromophenyl)-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3f): White solid 76% (82 mg), m.p. 109-111 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.57 – 7.49 (m, 2H), 7.47 – 7.38 (m, 1H), 7.34 – 7.21 (m, 3H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.53, 141.34, 135.89, 132.43, 131.81, 130.52, 129.14, 126.93, 125.11, 124.73, 84.41, 25.41. HRMS (ESI), calcd for $C_{16}H_{13}BrN_2O_3$ $[M+H]^+$ 362.0089, found 362.0088.



3g

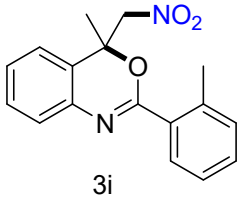
4-methyl-4-(nitromethyl)-2-(4-(trifluoromethyl)phenyl)-4H-benzo[d][1,3]oxazine (3g): White solid 55% (53 mg), m.p. 95-97 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.78 – 7.70 (m, 2H), 7.47 – 7.38 (m, 1H), 7.34 – 7.21 (m, 3H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.53, 141.34, 135.89, 132.43, 131.81, 130.52, 129.14, 126.93, 125.11, 124.73, 84.41, 25.41. HRMS (ESI), calcd for $C_{17}H_{13}F_3N_2O_3$ $[M+H]^+$ 351.0912, found 351.0911.



3h

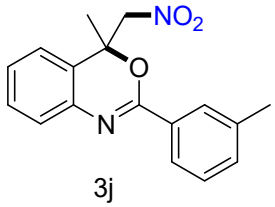
2-(4-(tert-butyl)phenyl)-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3h): Yellowish oil 82% (87 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H), 7.64 – 7.56 (m, 2H), 7.46 – 7.38 (m, 1H), 7.32 – 7.22 (m, 3H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 1.79 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.53, 155.35, 141.34, 135.89, 131.47, 129.14,

127.96, 126.12, 125.21, 125.00, 124.73, 84.41, 35.00, 31.09, 25.41. HRMS (ESI), calcd for $C_{20}H_{22}N_2O_3$ $[M+H]^+$ 339.1664, found 339.1665.



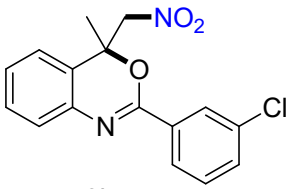
3i

4-methyl-4-(nitromethyl)-2-(o-tolyl)-4H-benzo[d][1,3]oxazine (3i): Yellowish oil 66% (59 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (ddd, *J* = 7.4, 1.2, 0.7 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.35 – 7.22 (m, 6H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 2.48 (d, *J* = 0.5 Hz, 3H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.03, 141.34, 137.35, 135.89, 134.61, 130.73, 129.24 (d, *J* = 19.1 Hz), 84.41, 25.41, 19.93. HRMS (ESI), calcd for $C_{17}H_{16}N_2O_3$ $[M+H]^+$ 297.1194, found 297.1193.



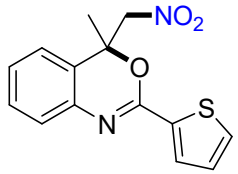
3j

4-methyl-4-(nitromethyl)-2-(m-tolyl)-4H-benzo[d][1,3]oxazine (3j): Yellowish oil 78% (82 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (ddd, *J* = 7.0, 2.2, 1.2 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.31 – 7.23 (m, 4H), 7.21 (t, *J* = 2.2 Hz, 1H), 7.16 (dd, *J* = 7.9, 7.1 Hz, 1H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 2.38 (d, *J* = 0.8 Hz, 3H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.59, 141.34, 139.07, 135.89, 134.09, 132.02, 129.04, 128.33, 125.21, 125.00, 124.73, 84.41, 25.41, 21.29. HRMS (ESI), calcd for $C_{17}H_{16}N_2O_3$ $[M+H]^+$ 297.1194, found 297.1193.



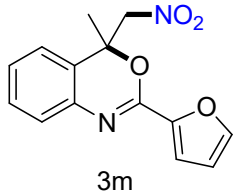
3k

2-(3-chlorophenyl)-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3k): Yellowish oil 69% (66.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (t, *J* = 2.3 Hz, 1H), 7.85 (ddd, *J* = 7.3, 2.2, 1.2 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.37 – 7.21 (m, 4H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.89, 135.25, 132.69, 130.78, 129.06, 128.62, 125.21, 125.00, 124.73, 84.41, 25.41. HRMS (ESI), calcd for $C_{16}H_{13}ClN_2O_3$ $[M+H]^+$ 318.0585, found 318.0586.



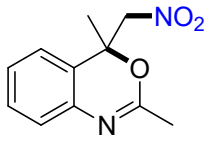
3l

4-methyl-4-(nitromethyl)-2-(thiophen-2-yl)-4H-benzo[d][1,3]oxazine (3l): Yellowish oil 75% (79 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 5.7, 1.8 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.32 – 7.23 (m, 3H), 7.06 (dd, *J* = 5.4, 1.8 Hz, 1H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.94, 141.34, 135.89, 130.70, 128.96, 127.83, 125.21, 125.00, 124.73, 120.12, 84.41, 25.41. HRMS (ESI), calcd for $C_{14}H_{12}N_2O_3S$ $[M+H]^+$ 289.0602, found 289.0604.



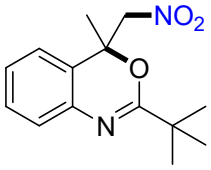
3m

2-(furan-2-yl)-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3m): White solid 71% (76 mg), m.p. 92-95 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (t, *J* = 1.7 Hz, 1H), 7.47 – 7.38 (m, 1H), 7.34 – 7.21 (m, 3H), 7.14 (dd, *J* = 4.4, 1.6 Hz, 1H), 6.74 (dd, *J* = 4.4, 1.6 Hz, 1H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.46, 143.04, 141.06, 135.89, 129.14, 125.21, 125.00, 124.73, 118.83, 113.17, 84.40, 25.41. HRMS (ESI), calcd for $C_{14}H_{12}N_2O_4$ $[M+H]^+$ 273.0831, found 273.0830.



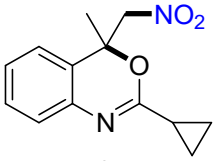
3n

2,4-dimethyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3n): Yellowish oil 68% (55 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 1H), 7.32 – 7.21 (m, 3H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 2.07 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.81, 142.72, 132.88, 128.92, 124.64, 123.42, 84.41, 25.41, 20.13. HRMS (ESI), calcd for $C_{11}H_{12}N_2O_3$ $[M+H]^+$ 221.0881, found 221.0882.



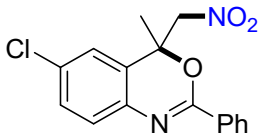
3o

2-(tert-butyl)-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3o): Yellowish oil 72% (68 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 1H), 7.34 – 7.21 (m, 3H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 10H), 1.79 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.83, 141.34, 135.89, 129.14, 125.11, 124.73, 84.41, 35.68, 27.76, 25.41. HRMS (ESI), calcd for $C_{14}H_{18}N_2O_3$ $[M+H]^+$ 263.1351, found 263.1350.



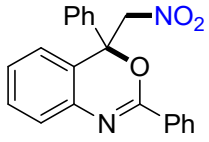
3p

2-cyclopropyl-4-methyl-4-(nitromethyl)-4H-benzo[d][1,3]oxazine (3p): Yellow oil 59% (46 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 1H), 7.34 – 7.21 (m, 3H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 1.79 (s, 3H), 0.77 – 0.61 (m, 2H), 0.52 – 0.36 (m, 2H), 0.20 (p, *J* = 5.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.68, 141.69, 134.83, 129.05, 124.83, 124.46, 84.41, 25.41, 15.85, 8.54. HRMS (ESI), calcd for $C_{13}H_{14}N_2O_3$ $[M+H]^+$ 247.1038, found 247.1039.



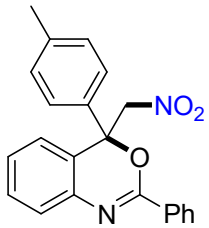
3q

6-chloro-4-methyl-4-(nitromethyl)-2-phenyl-4H-benzo[d][1,3]oxazine (3q): Yellowish oil 67% (61 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.1, 1.7 Hz, 2H), 7.58 – 7.44 (m, 3H), 7.42 – 7.37 (m, 1H), 7.34 – 7.26 (m, 2H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.2 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.53, 141.78, 132.48, 131.87, 131.15, 129.12, 128.99, 127.14, 125.45, 84.41, 25.41. HRMS (ESI), calcd for $C_{16}H_{13}ClN_2O_3$ $[M+H]^+$ 318.0585, found 318.0586.



3r

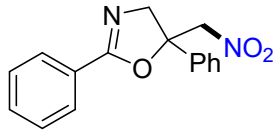
4-(nitromethyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine (3r): White solid 82% (87 mg), m.p. 102-105 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.58 – 7.47 (m, 7H), 7.44 – 7.40 (m, 1H), 7.33 – 7.23 (m, 3H), 7.18 (tt, *J* = 6.3, 1.6 Hz, 1H), 5.30 (d, *J* = 14.8 Hz, 1H), 5.05 (d, *J* = 14.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.64, 143.47, 131.15, 129.82, 129.10, 128.28, 127.28, 126.52, 125.04, 124.21, 123.34, 88.52, HRMS (ESI), calcd for $C_{21}H_{16}N_2O_3$ $[M+H]^+$ 345.1194, found 345.1193.



3s

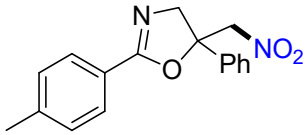
4-(nitromethyl)-2-phenyl-4-(p-tolyl)-4H-benzo[d][1,3]oxazine (3s): White solid 78% (76.5 mg), m.p. 94-96 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 2H), 7.58 – 7.44 (m, 3H), 7.49 – 7.38 (m, 1H), 7.32 – 7.21 (m, 3H), 7.22 – 7.14 (m, 2H), 6.89 – 6.81 (m, 2H), 5.30 (d, *J* = 14.8 Hz, 1H), 5.05 (d, *J* = 14.8 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.64,

143.95, 141.47, 137.34, 132.48, 131.15, 129.82, 128.99, 128.45, 126.91, 125.04, 124.21, 123.34, 88.52, 21.19. HRMS (ESI), calcd for $C_{22}H_{18}N_2O_3$ $[M+H]^+$ 359.1351, found 359.1352.



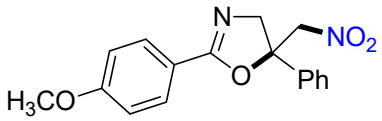
5a

5-(nitromethyl)-2,5-diphenyl-4,5-dihydrooxazole (5a): Yellow oil 73% (71.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.3, 1.6 Hz, 2H), 7.58 – 7.47 (m, 3H), 7.39 (t, *J* = 7.3 Hz, 2H), 6.92 – 6.88 (m, 1H), 6.75 (dd, *J* = 7.6, 6.4 Hz, 2H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.5 Hz, 1H), 4.10 (d, *J* = 12.5 Hz, 1H), 3.85 (d, *J* = 12.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.88, 135.06, 131.15, 128.88, 127.92, 126.91, 126.55, 125.68, 87.26, 63.67. HRMS (ESI), calcd for $C_{16}H_{14}N_2O_3$ $[M+H]^+$ 283.1038, found 283.1037.



5b

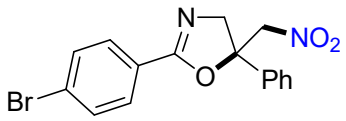
5-(nitromethyl)-5-phenyl-2-(p-tolyl)-4,5-dihydrooxazole (5b): Yellow oil 78% (82 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.9 Hz, 2H), 7.51 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.24 (dd, *J* = 7.8, 0.9 Hz, 2H), 6.94 – 6.86 (m, 1H), 6.79 – 6.70 (m, 2H), 4.96 (d, *J* = 14.2 Hz, 1H), 4.71 (d, *J* = 14.4 Hz, 1H), 4.10 (d, *J* = 12.5 Hz, 1H), 3.85 (d, *J* = 12.4 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.88, 141.89, 135.06, 129.34, 127.92, 127.25, 126.91, 125.68, 87.26, 63.67, 21.42. HRMS (ESI), calcd for $C_{17}H_{16}N_2O_3$ $[M+H]^+$ 297.1194, found 297.1193.



5c

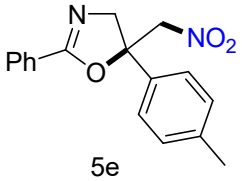
2-(4-methoxyphenyl)-5-(nitromethyl)-5-phenyl-4,5-dihydrooxazole (5c): Yellow oil 81% (85 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 7.6, 1.4 Hz, 2H), 6.94 – 6.86 (m, 3H), 6.79 – 6.70 (m, 2H), 4.96 (d, *J* = 14.3 Hz, 1H), 4.71 (dd, *J* = 14.5, 0.7 Hz, 1H),

4.10 (d, J = 12.5 Hz, 1H), 3.85 (d, J = 12.5 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.98, 160.88, 135.06, 127.90, 126.91, 126.21, 125.68, 114.58, 87.26, 63.67, 55.35. HRMS (ESI), calcd for $C_{17}H_{16}N_2O_3$ $[M+H]^+$ 313.1144, found 313.1143.



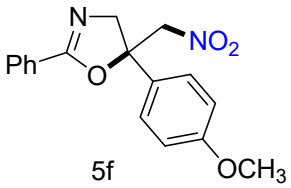
5d

2-(4-bromophenyl)-5-(nitromethyl)-5-phenyl-4,5-dihydrooxazole (5d): Yellow oil 83% (86 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 2H), 7.55 – 7.49 (m, 4H), 6.92 – 6.88 (m, 1H), 6.75 (dd, J = 7.6, 6.5 Hz, 2H), 4.96 (d, J = 14.1 Hz, 1H), 4.71 (d, J = 14.5 Hz, 1H), 4.10 (d, J = 12.5 Hz, 1H), 3.85 (d, J = 12.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.88, 135.06, 132.41, 129.17, 127.92, 126.92, 125.68, 87.26, 63.67. HRMS (ESI), calcd for $C_{16}H_{13}BrN_2O_3$ $[M+H]^+$ 362.0089, found 362.0088.



5e

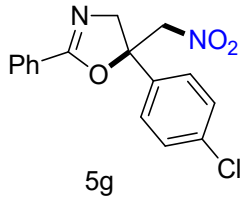
5-(nitromethyl)-2-phenyl-5-(p-tolyl)-4,5-dihydrooxazole (5e): Yellow oil 82% (81 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.3, 1.6 Hz, 2H), 7.58 – 7.49 (m, 1H), 7.43 – 7.30 (m, 14H), 7.14 – 7.08 (m, 2H), 4.96 (d, J = 14.2 Hz, 1H), 4.71 (d, J = 14.5 Hz, 1H), 4.10 (d, J = 12.6 Hz, 1H), 3.85 (d, J = 12.6 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.88, 137.11, 134.61, 131.15, 129.22, 128.88, 126.55, 124.08, 87.26, 63.67, 21.19. HRMS (ESI), m/z calcd for $C_{17}H_{16}N_2O_3$ $[M+H]^+$ 297.1194, found 297.1195.



5f

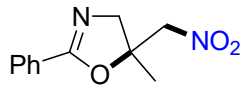
5-(4-methoxyphenyl)-5-(nitromethyl)-2-phenyl-4,5-dihydrooxazole (5f): Yellow oil 71% (69 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.3, 1.6 Hz, 2H), 7.58 – 7.49 (m, 3H), 7.42 –

7.36 (m, 2H), 6.82 (d, J = 8.5 Hz, 2H), 4.96 (d, J = 14.3 Hz, 1H), 4.71 (d, J = 14.5 Hz, 1H), 4.10 (d, J = 12.5 Hz, 1H), 3.85 (d, J = 12.5 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.88, 158.88, 132.16, 131.15, 128.88, 126.55, 126.06, 113.71, 87.26, 63.67, 55.35. HRMS (ESI), calcd for $C_{17}H_{16}N_2O_4$ $[M+H]^+$ 313.1144, found 313.1145.



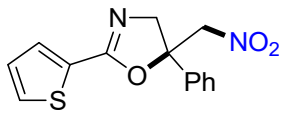
5g

5-(4-chlorophenyl)-5-(nitromethyl)-2-phenyl-4,5-dihydrooxazole (5g): Yellow oil 82% (87 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.3, 1.6 Hz, 2H), 7.58 – 7.49 (m, 1H), 7.42 – 7.32 (m, 4H), 7.30 – 7.25 (m, 2H), 4.96 (d, J = 14.1 Hz, 1H), 4.71 (d, J = 14.5 Hz, 1H), 4.10 (d, J = 12.6 Hz, 1H), 3.85 (d, J = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, C $CDCl_3$) δ 160.88, 134.12, 132.74, 131.15, 128.88, 128.36, 126.66, 87.26, 63.67. HRMS (ESI), calcd for $C_{16}H_{13}ClN_2O_3$ $[M+H]^+$ 318.0585, found 318.0584.



5h

5-(nitromethyl)-5-phenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (5h): Yellow oil 35% (42 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.3, 1.6 Hz, 2H), 7.58 – 7.49 (m, 1H), 7.43 – 7.34 (m, 2H), 4.61 (d, J = 13.7 Hz, 1H), 4.36 (d, J = 13.9 Hz, 1H), 3.75 (d, J = 12.3 Hz, 1H), 3.50 (d, J = 12.3 Hz, 1H), 1.50 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.10, 131.14, 128.87, 126.54, 94.36, 87.58, 70.93, 23.49. HRMS (ESI), calcd for $C_{11}H_{12}N_2O_3$ $[M+H]^+$ 221.0881, found 221.0882.



5i

5-(nitromethyl)-5-phenyl-2-(thiophen-2-yl)-4,5-dihydrooxazole (5i): Yellow oil 65% (72 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (dd, J = 5.7, 1.8 Hz, 1H), 7.51 (dd, J = 7.6, 1.5 Hz, 2H), 7.44 (t, J = 5.6 Hz, 1H), 7.06 (dd, J = 5.4, 1.8 Hz, 1H), 6.94 – 6.86 (m, 1H), 6.75 (dd, J = 7.6, 6.5 Hz,

2H), 4.96 (d, J = 14.1 Hz, 1H), 4.71 (d, J = 14.5 Hz, 1H), 1.90 (d, J = 12.5 Hz, 1H), 1.60 (d, J = 12.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.95, 135.06, 130.70, 127.92, 127.83, 126.91, 126.40, 125.68, 125.62, 87.31, 62.31. HRMS (ESI), calcd for $C_{14}H_{12}N_2O_3S$ $[M+H]^+$ 288.0569, found 288.0568.

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2. (a) H. Yang, X.-H. Duan, J.-F. Zhao L. N. Guo, *Org. Lett*. 2015, **17**, 1998-2001. (b) Q. H. Deng, J.-R. Chen, Q. Wei, Q.-Q. hao, L. –Q. Lu W.-J. Xiao, *Chem. Commun*. 2015, **51**, 3537-3540. (c) T. Qian, Q. Jiang, J. Ji, J. Luo, X. Zhao, *Org. Biomol. Chem*. 2019, **17**, 1763-1766.

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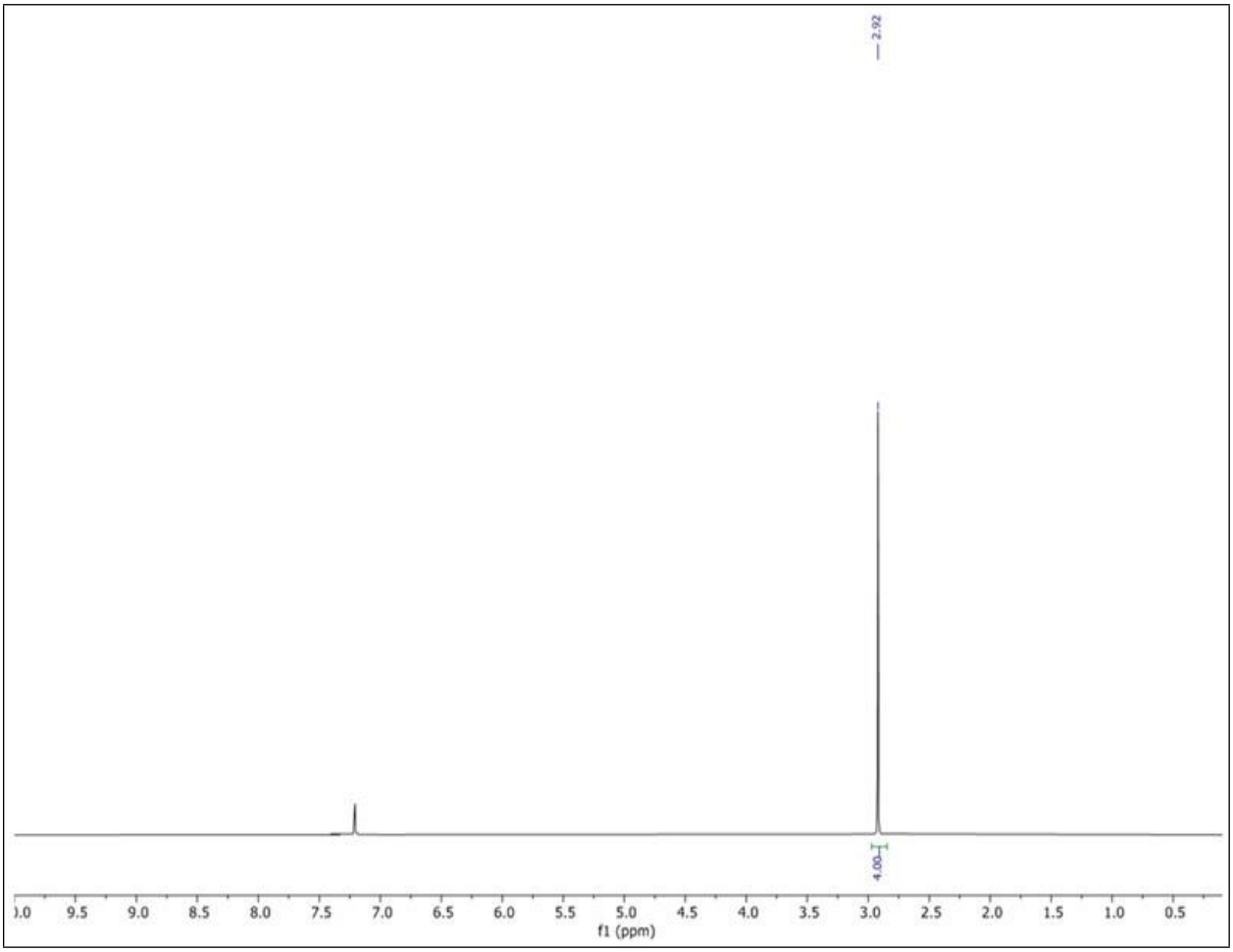

Figure S1. ^{1}H NMR spectra of **2** in $CDCl_3$.

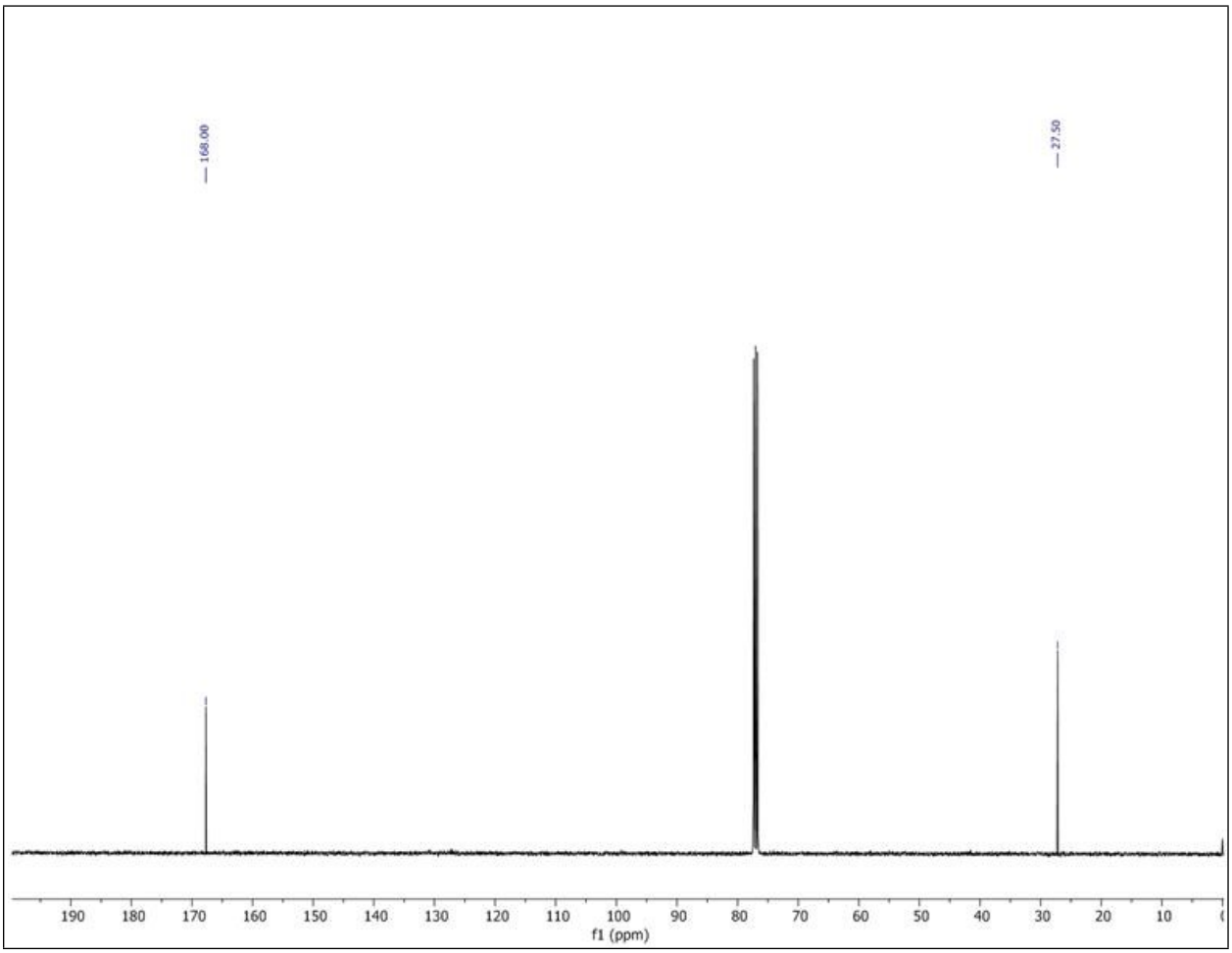

Figure S2. ^{13}C NMR spectra of **2** in $CDCl_3$.

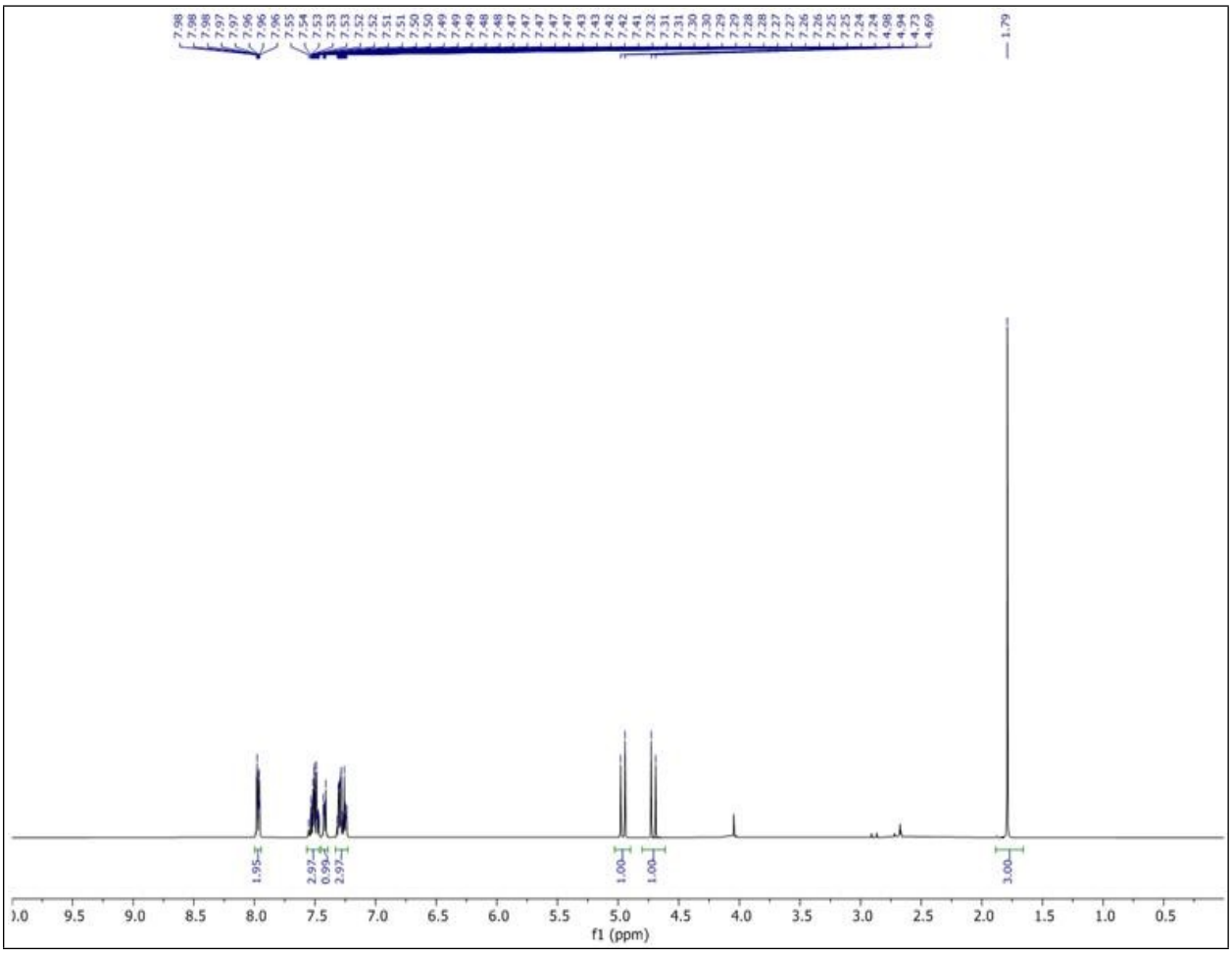

Figure S3. ^{1}H NMR spectra of **3a** in $CDCl_3$.

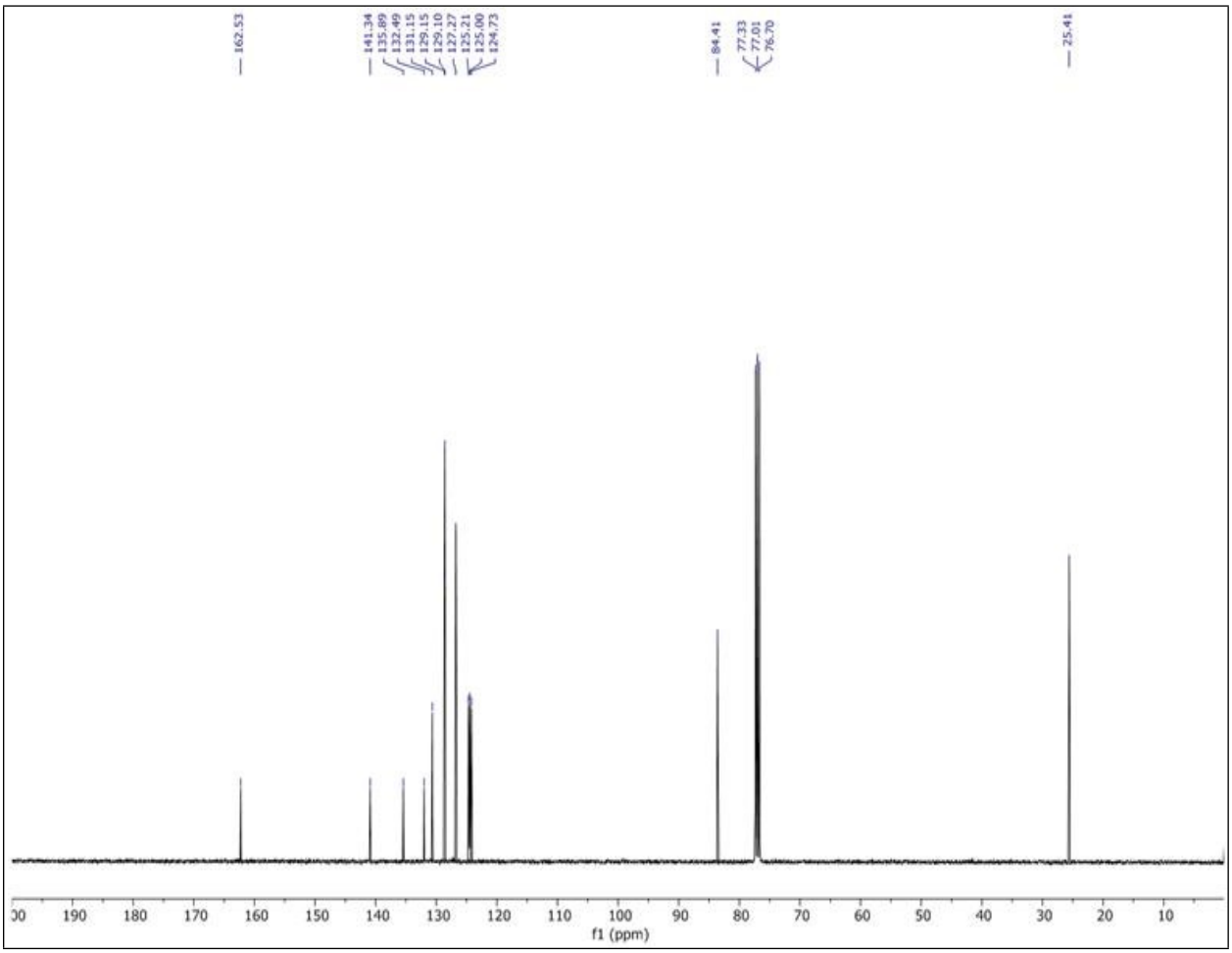

Figure S4. ^{13}C NMR spectra of **3a** in $CDCl_3$.

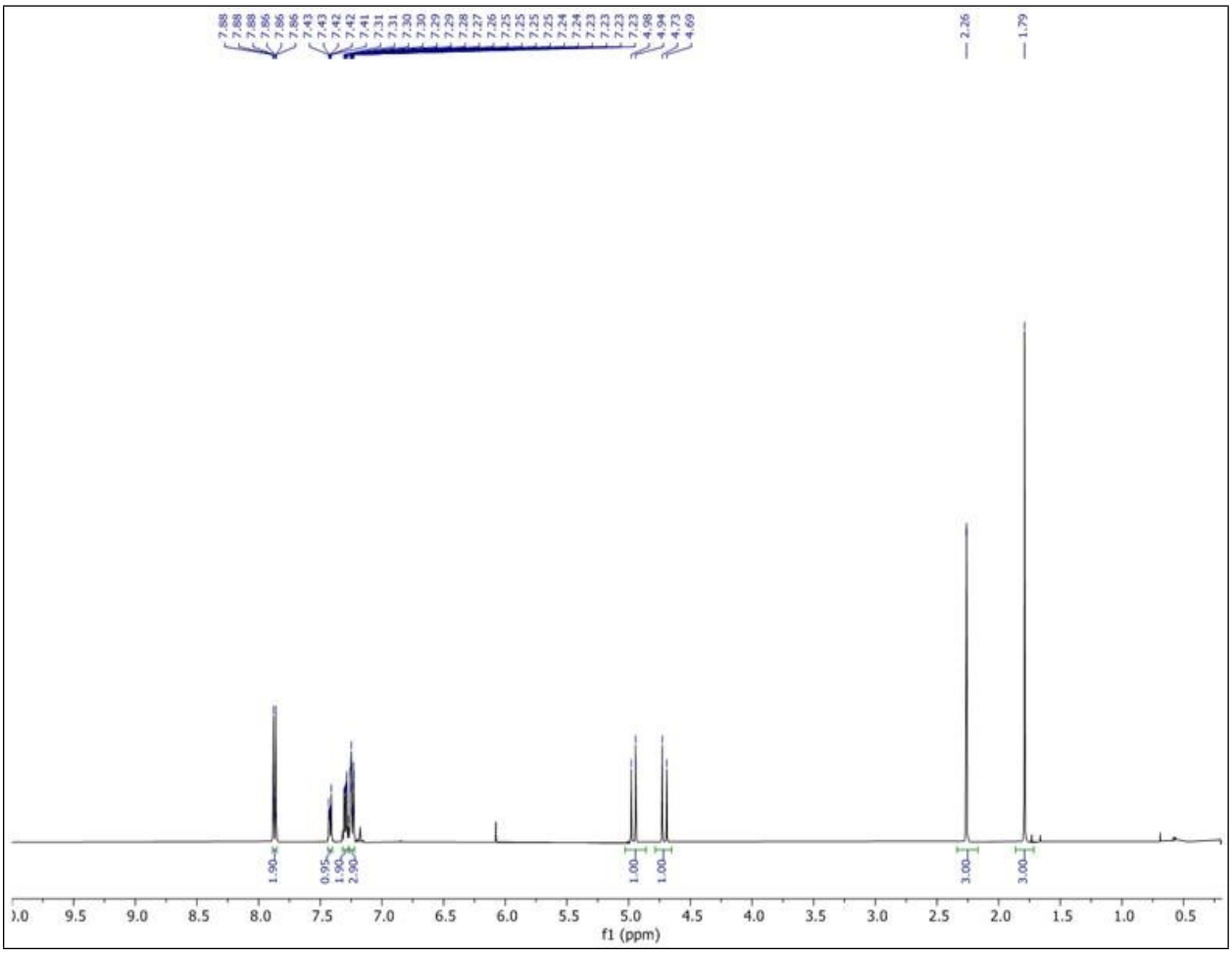

Figure S5. ^{1}H NMR spectra of **3b** in $CDCl_3$.

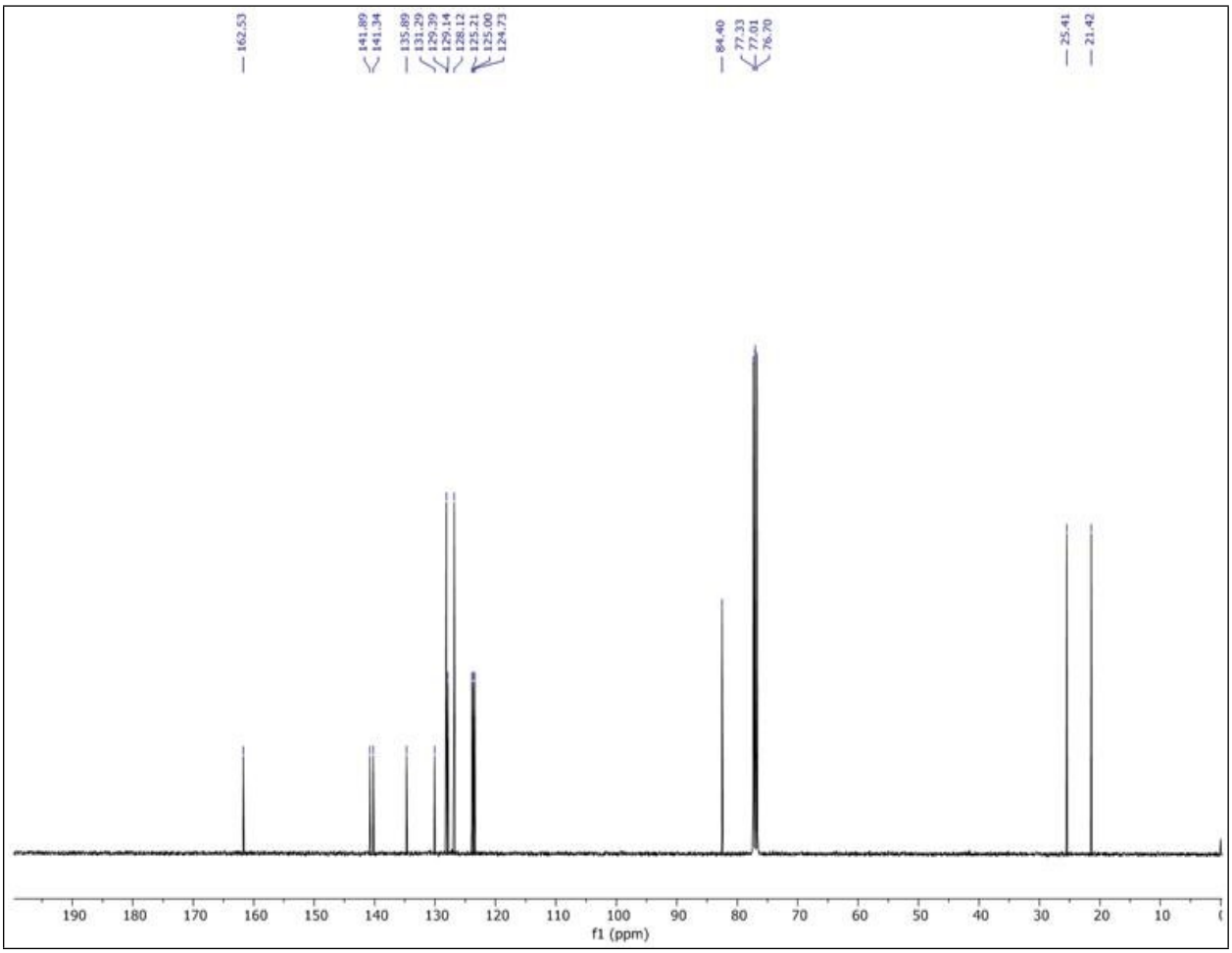

Figure S6. ^{13}C NMR spectra of **3b** in $CDCl_3$.

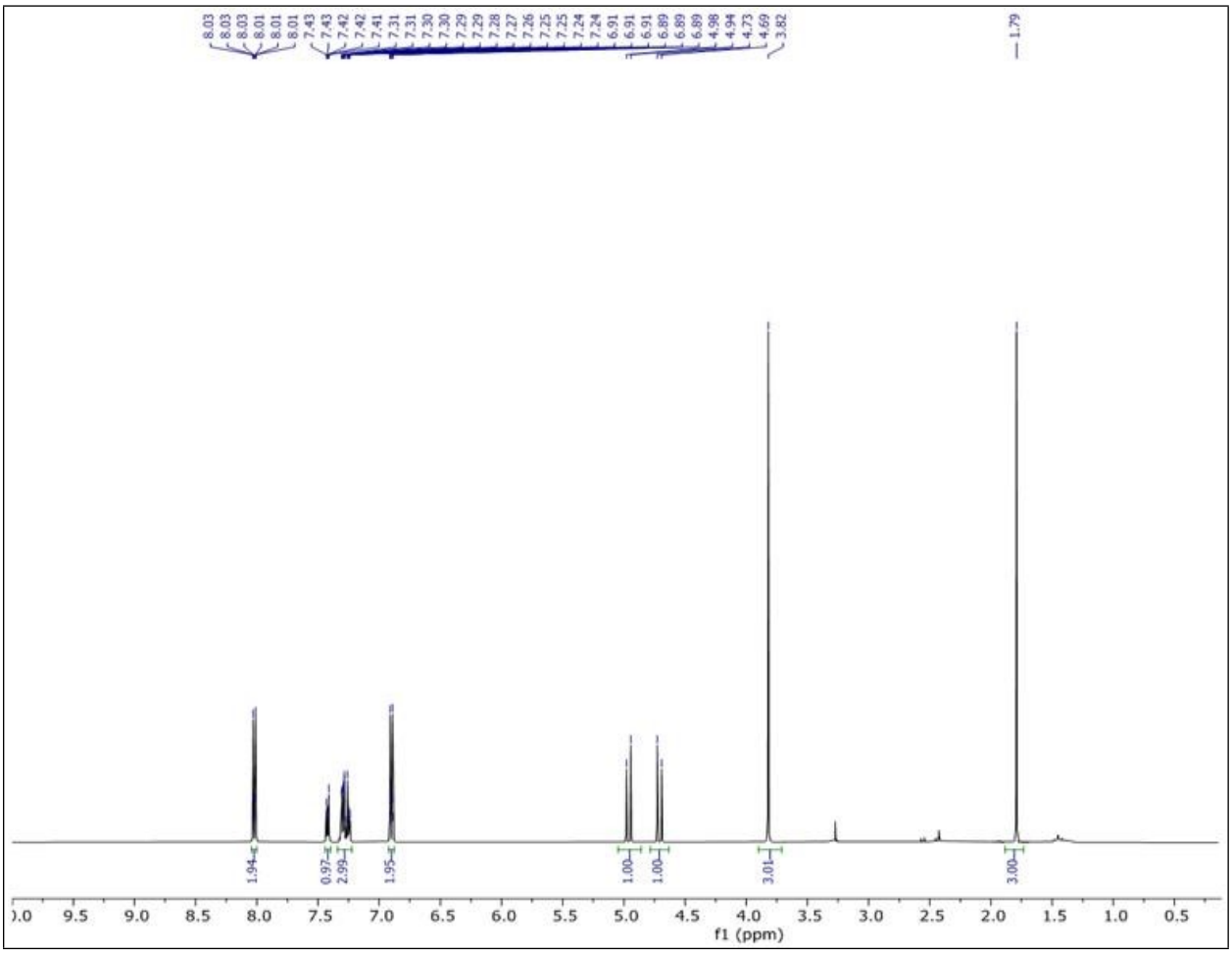

Figure S7. ^{1}H NMR spectra of **3c** in $CDCl_3$.

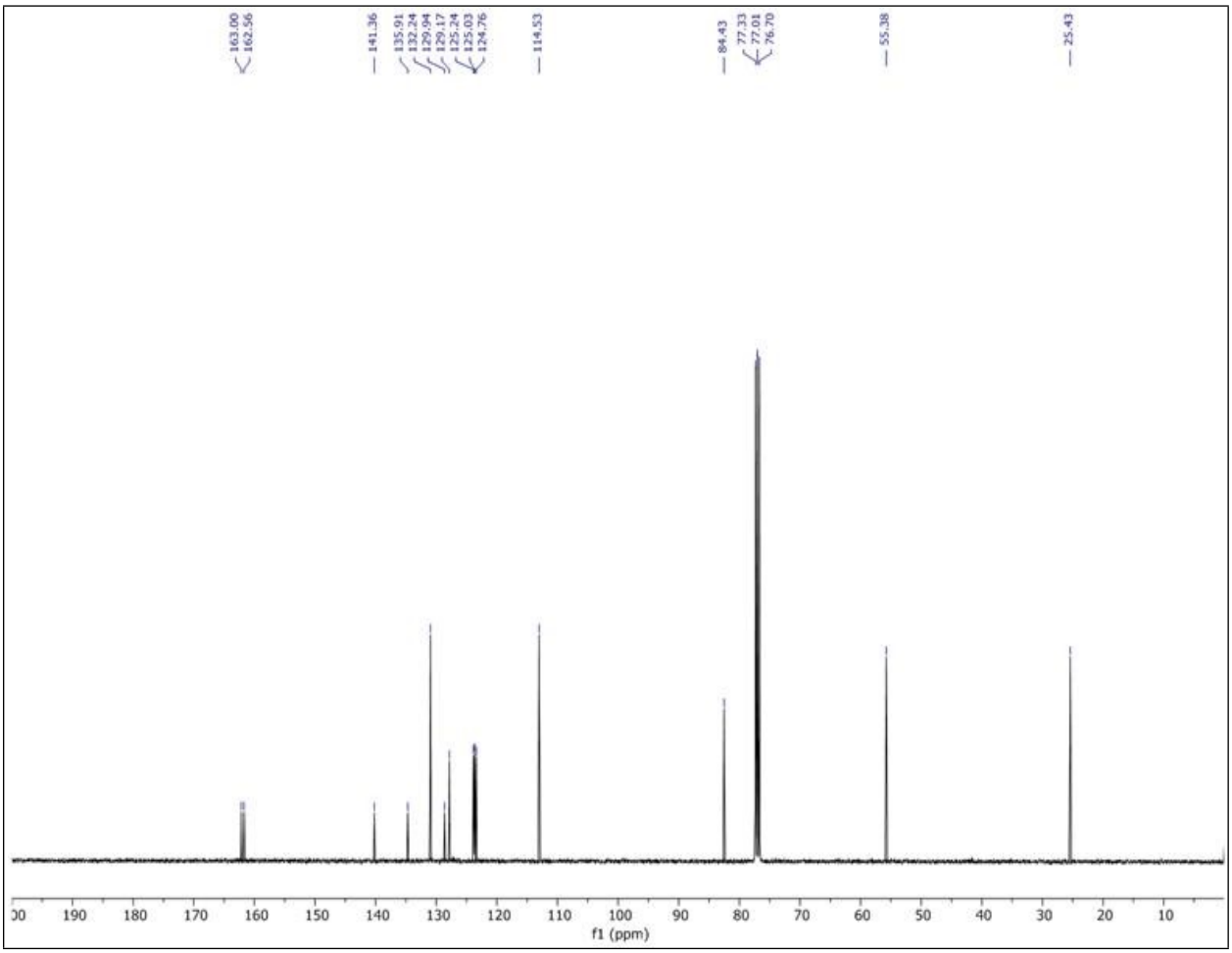

Figure S8. ^{13}C NMR spectra of **3c** in $CDCl_3$.

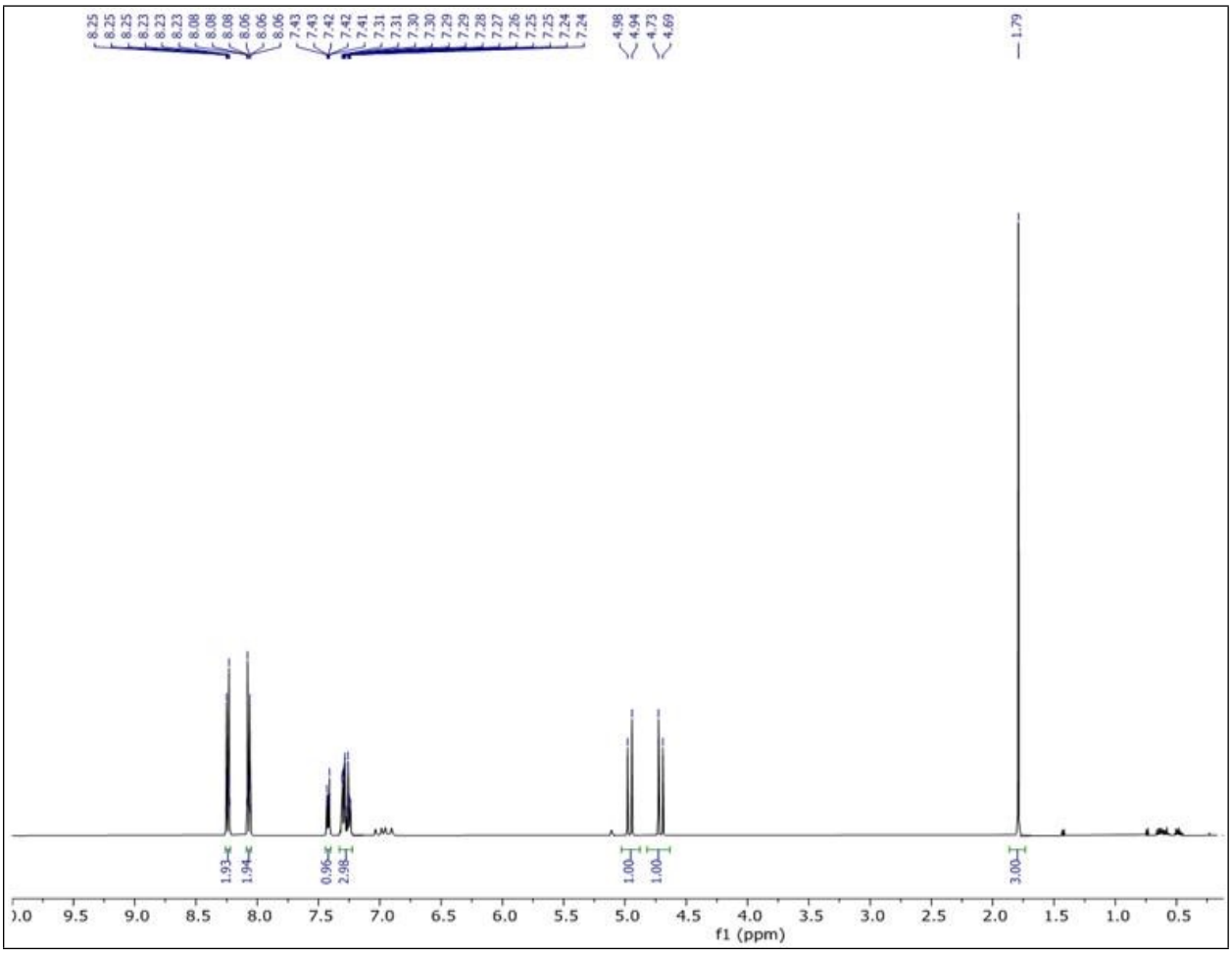

Figure S9. ^{1}H NMR spectra of **3d** in $CDCl_3$.

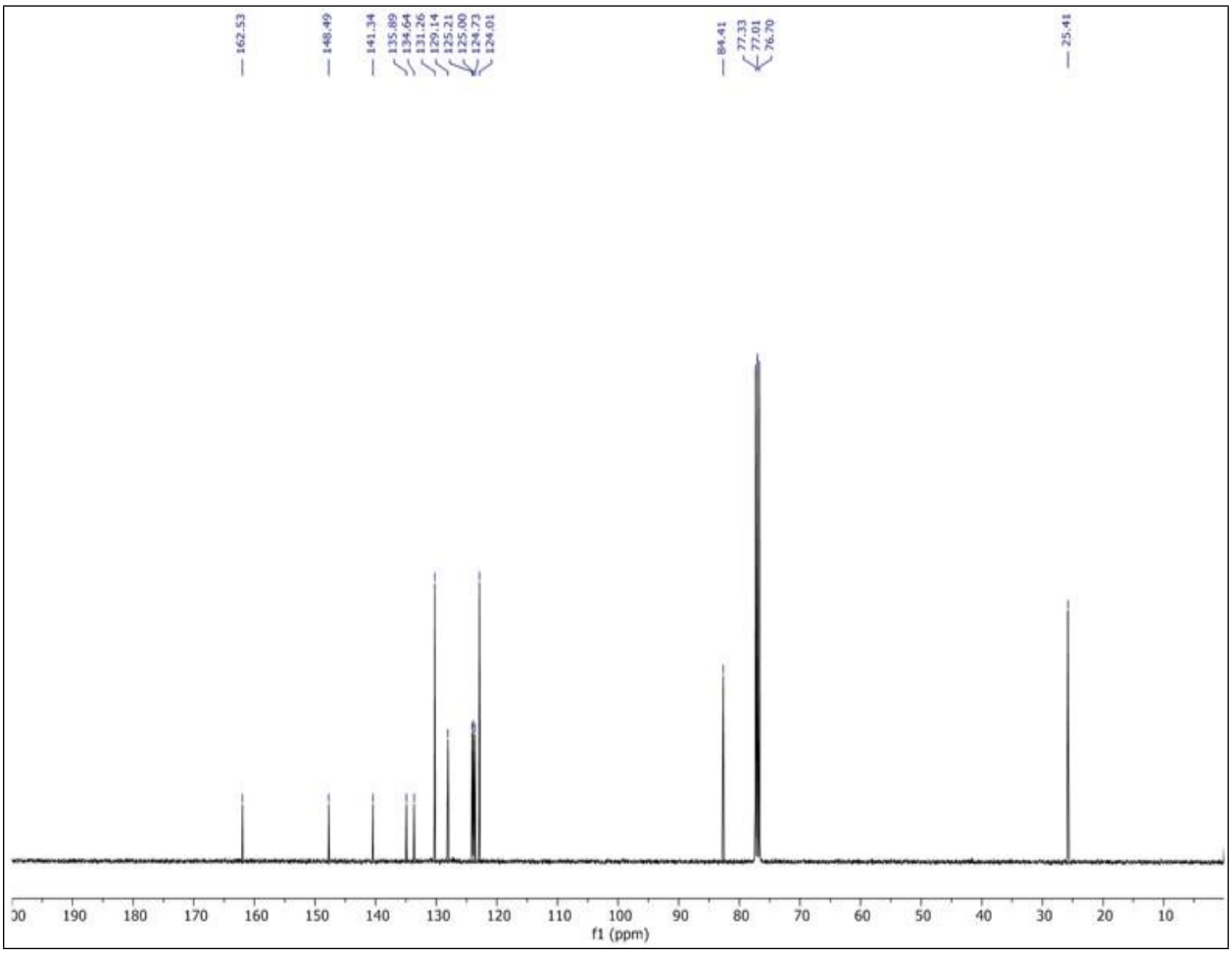

Figure S10. ^{13}C NMR spectra of **3d** in $CDCl_3$.

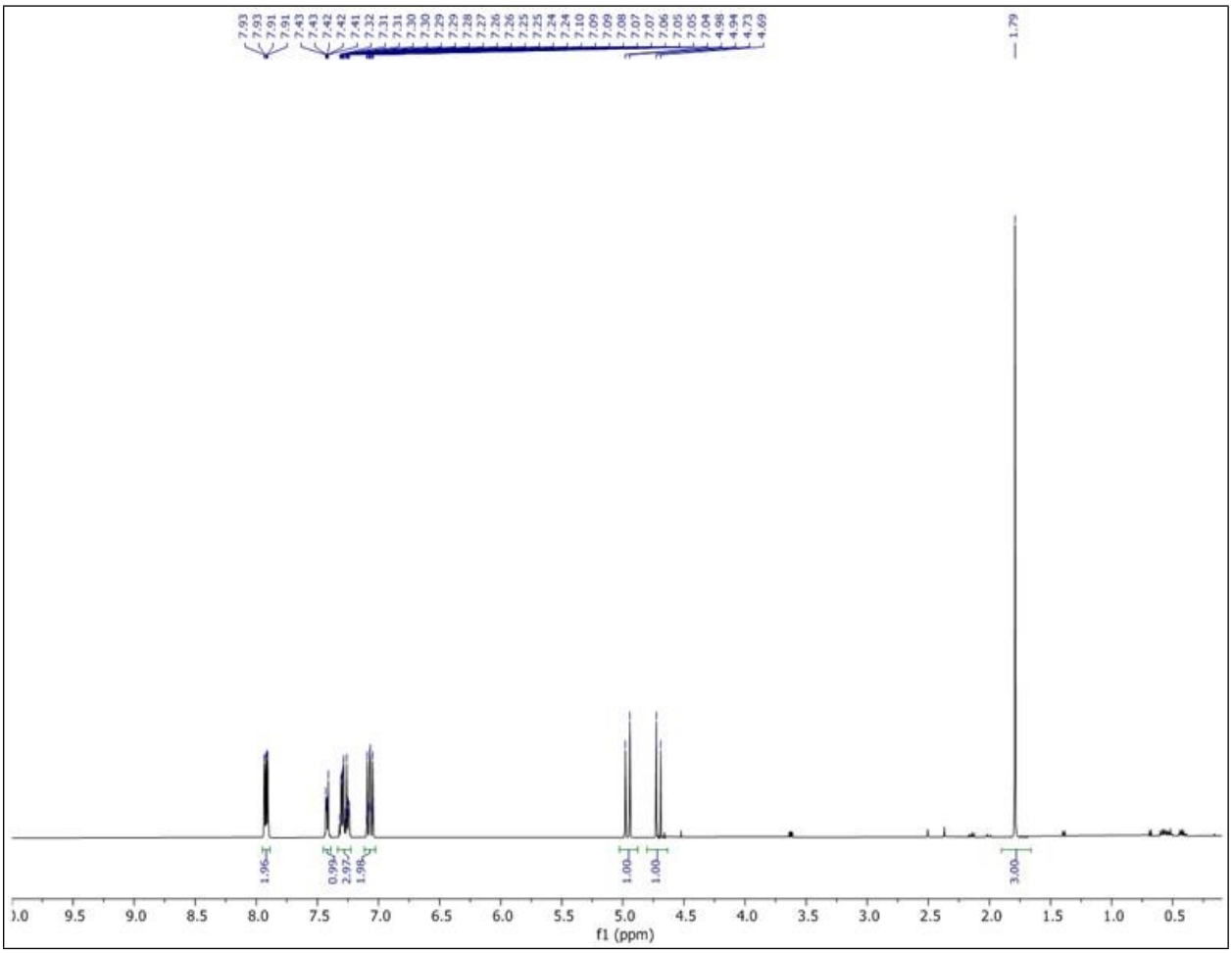

Figure S11. ^{1}H NMR spectra of **3e** in $CDCl_3$.

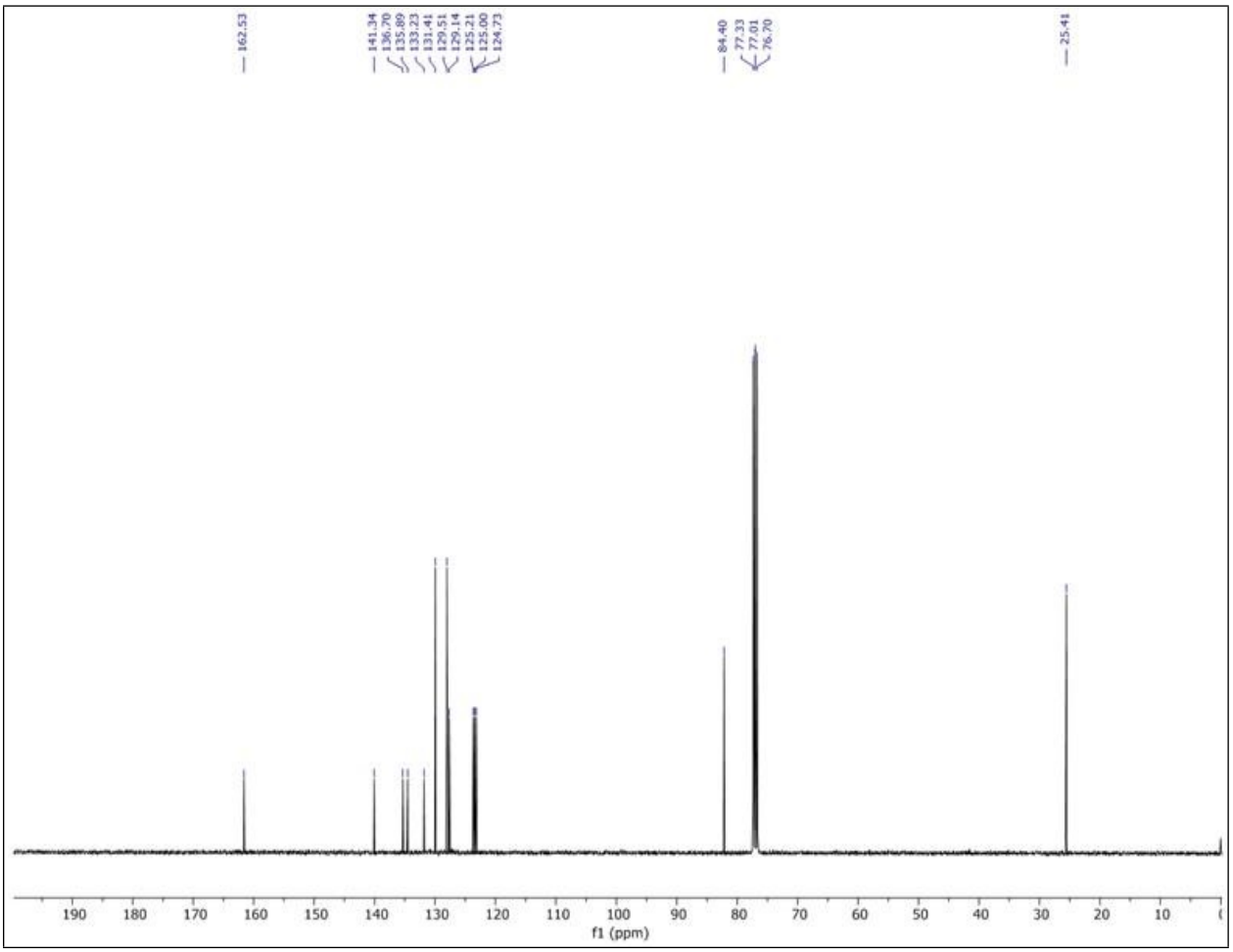

Figure S12. ^{13}C NMR spectra of **3e** in $CDCl_3$.

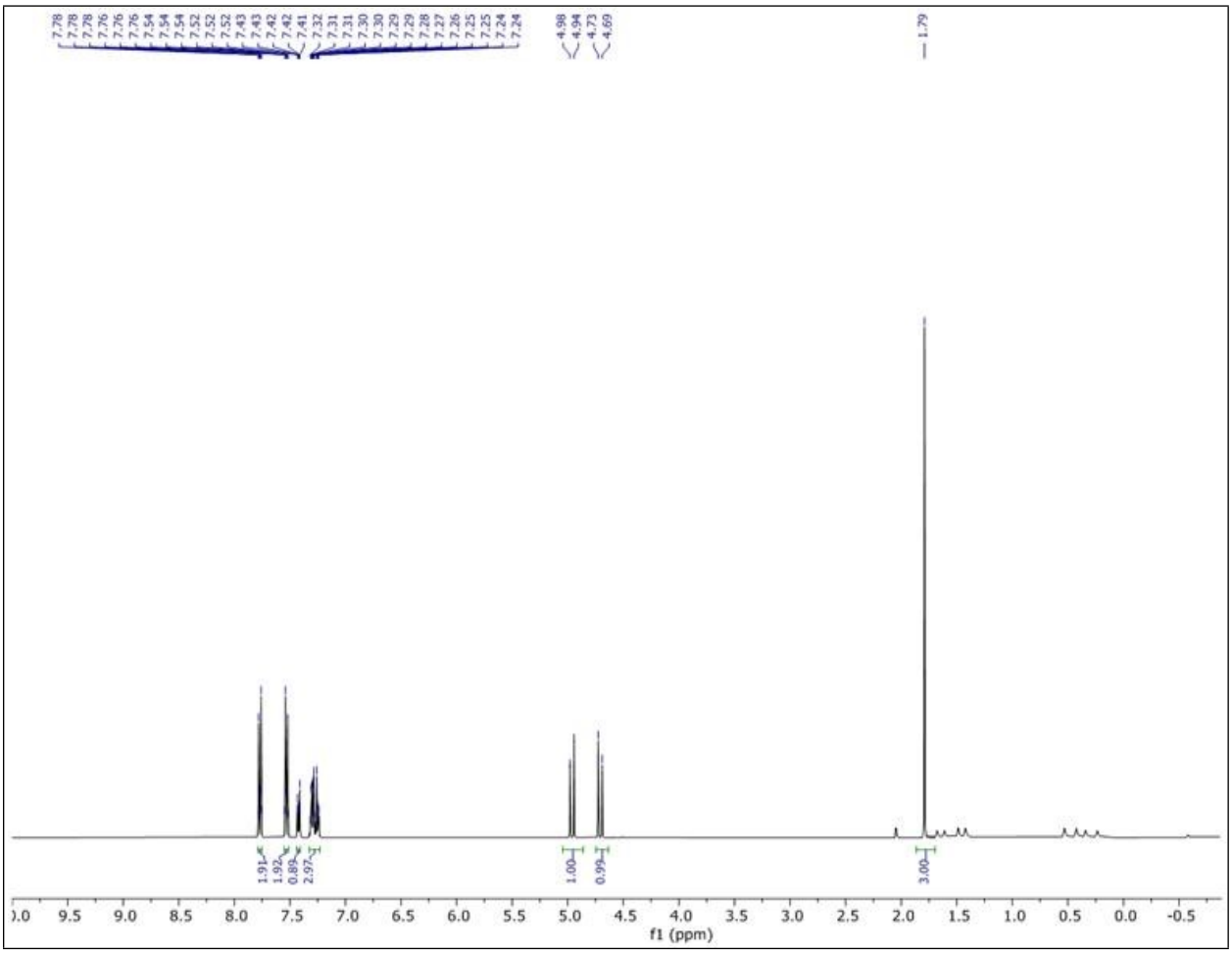

Figure S13. ^{1}H NMR spectra of **3f** in $CDCl_3$.

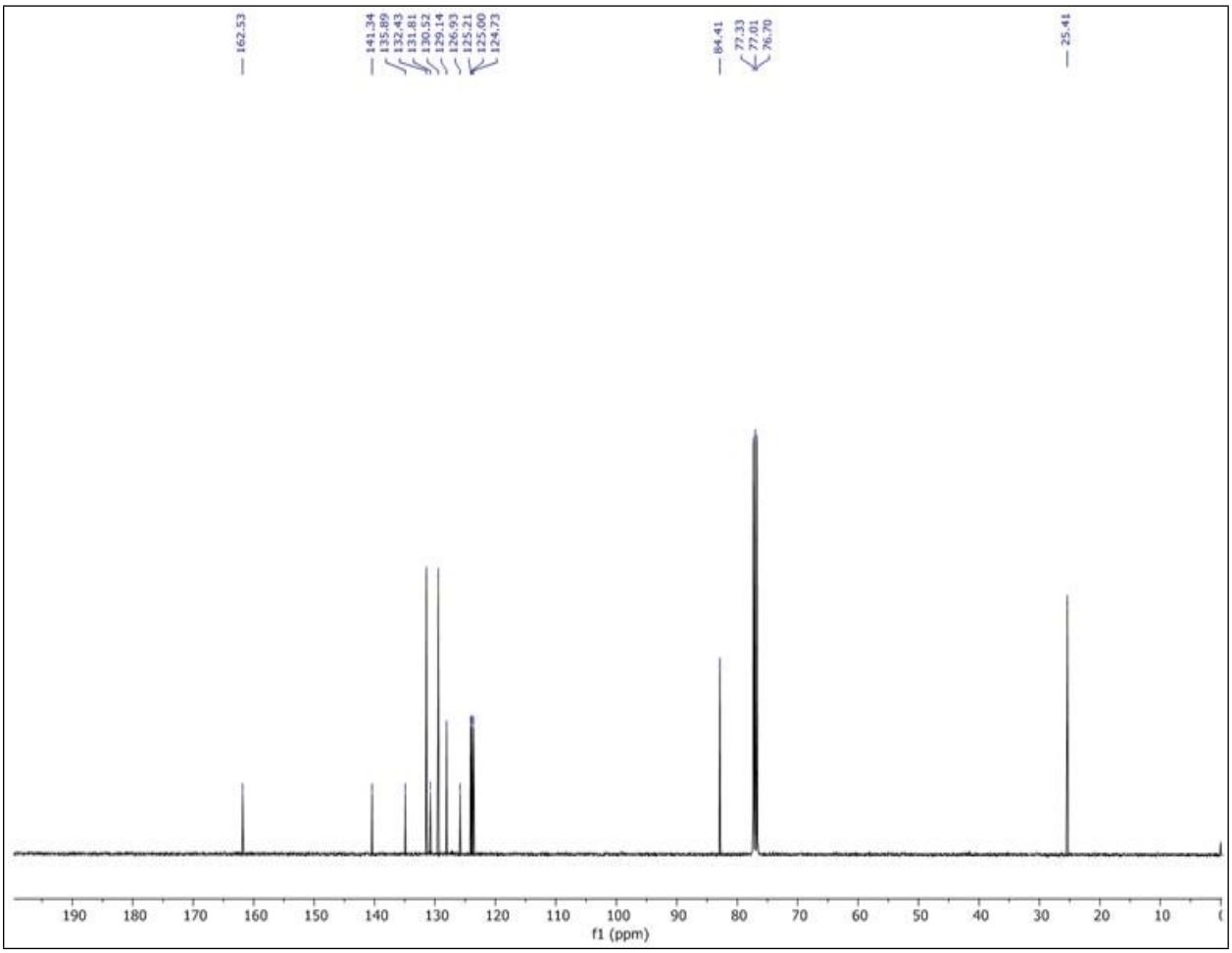

Figure S14. ^{13}C NMR spectra of **3f** in $CDCl_3$.

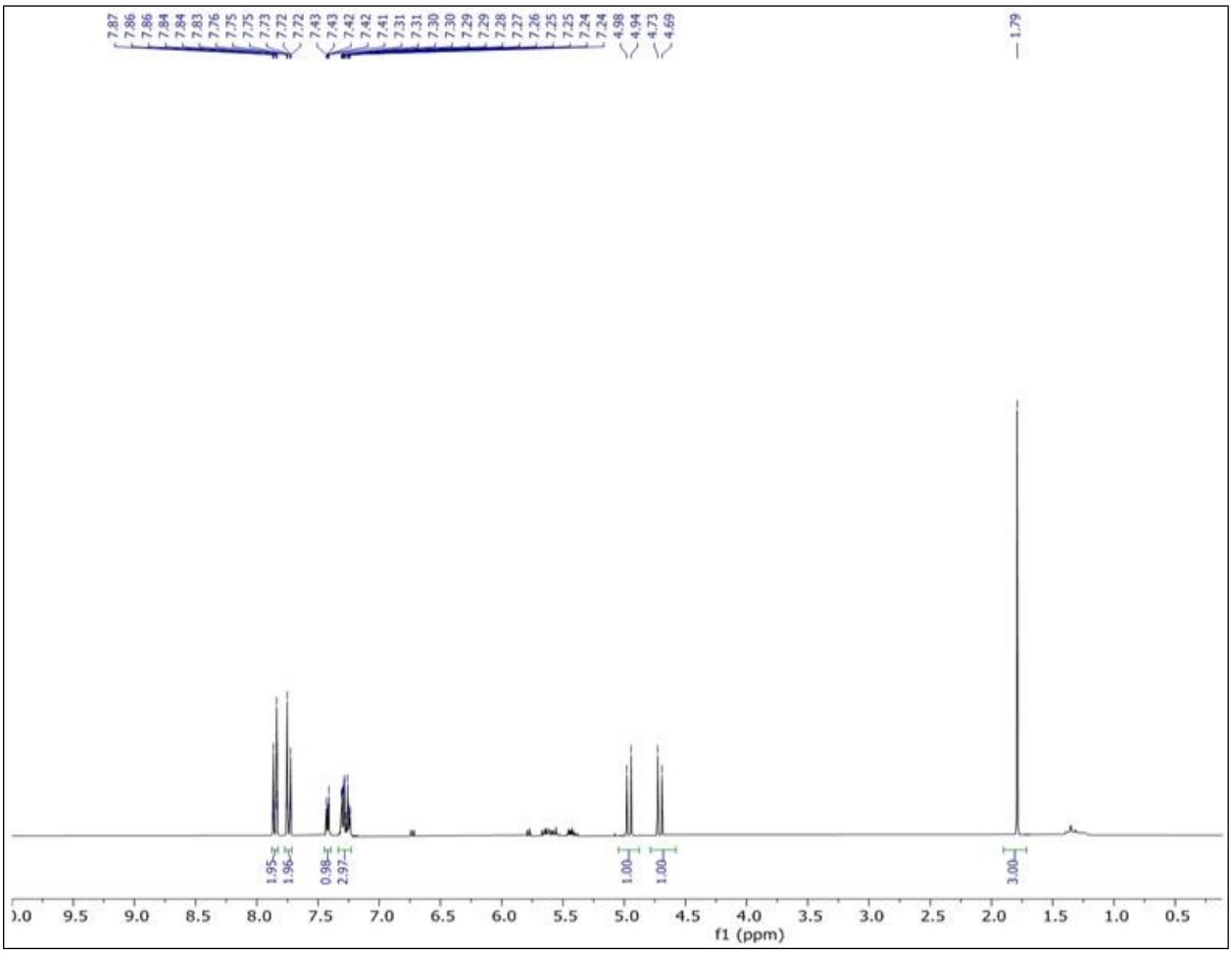

Figure S15. ^{1}H NMR spectra of **3g** in $CDCl_3$.

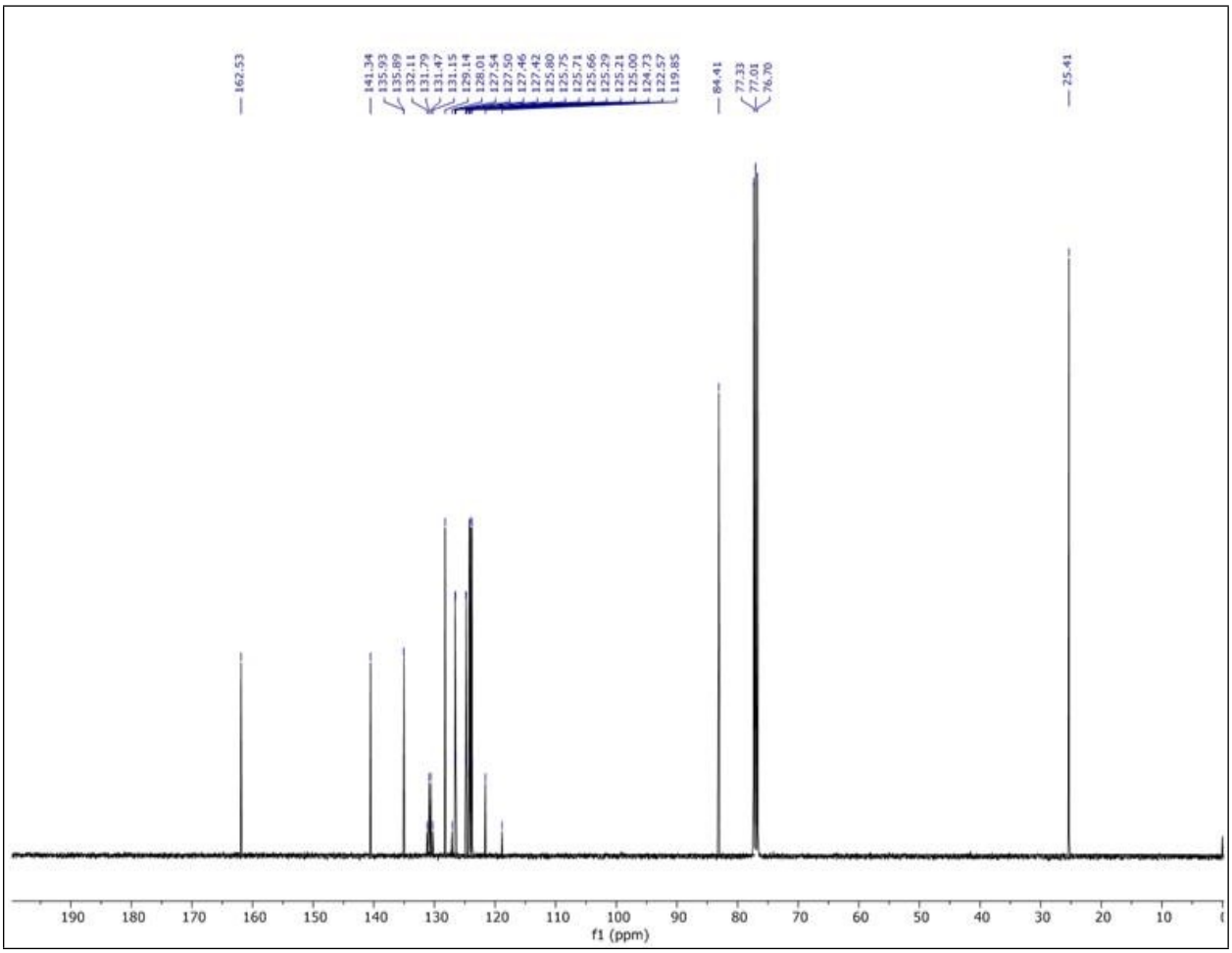

Figure S16. ^{13}C NMR spectra of **3g** in $CDCl_3$.

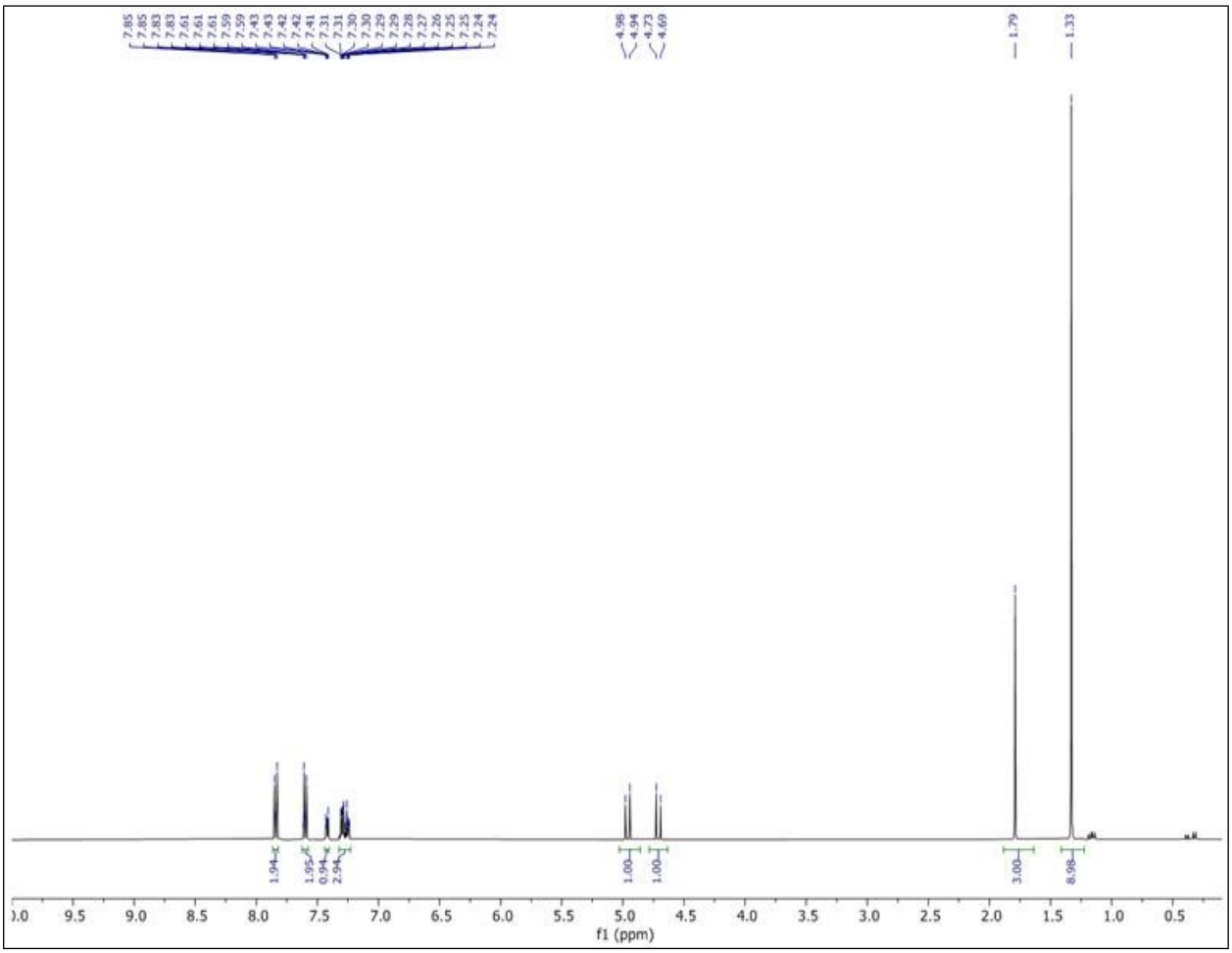

Figure S17. ^{1}H NMR spectra of **3h** in $CDCl_3$.

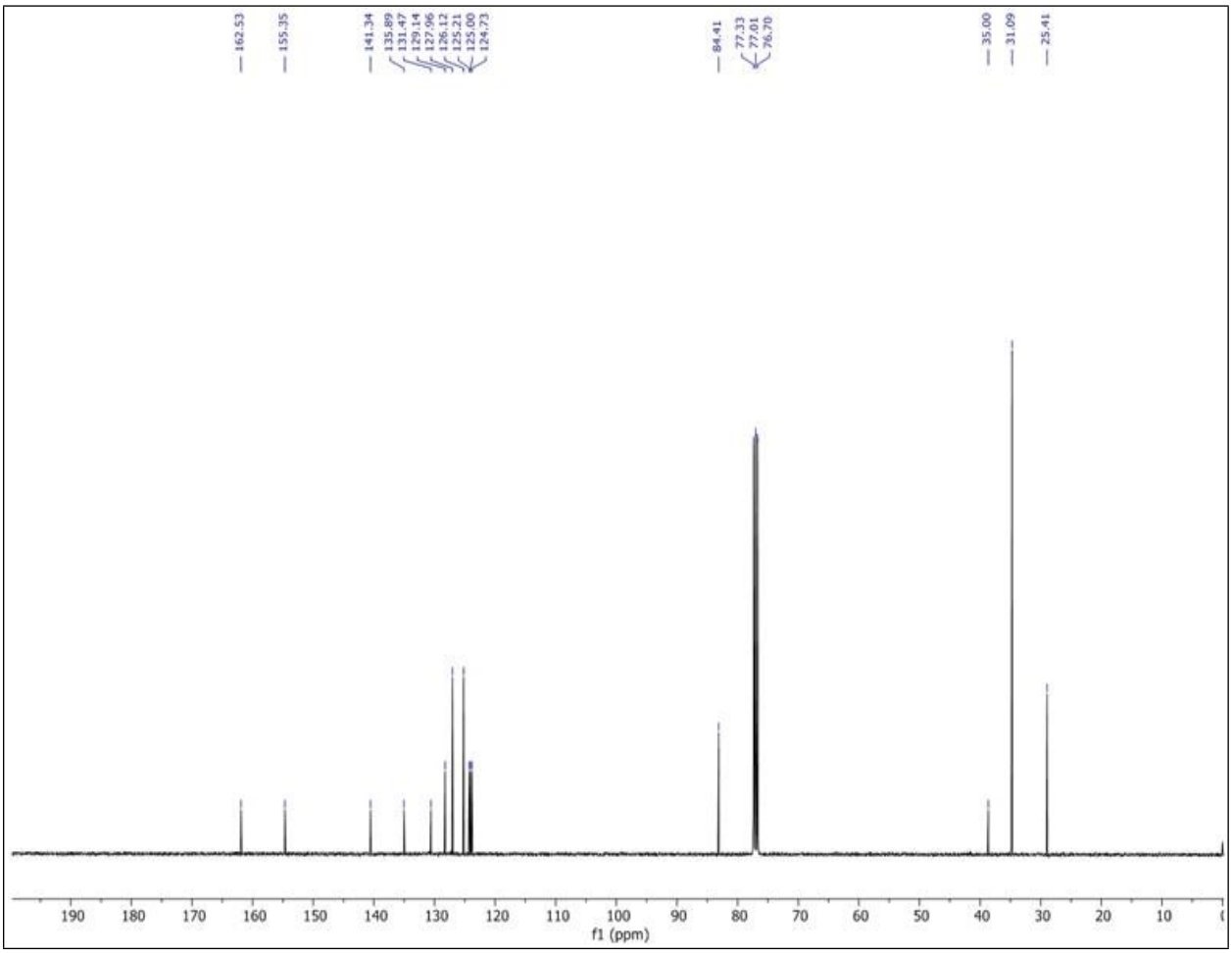

Figure S18. ^{13}C NMR spectra of **3h** in $CDCl_3$.

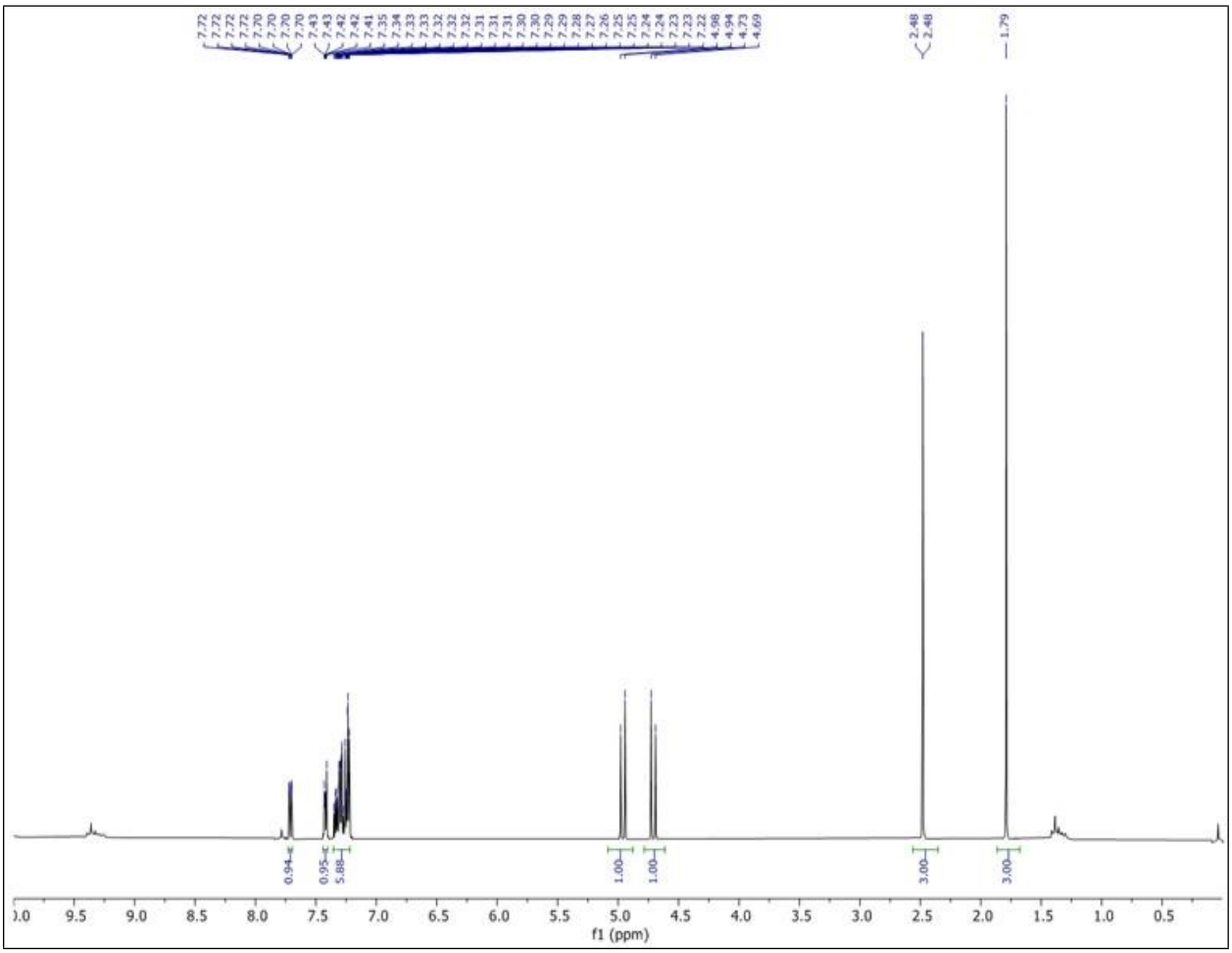

Figure S19. ^{1}H NMR spectra of **3i** in $CDCl_3$.

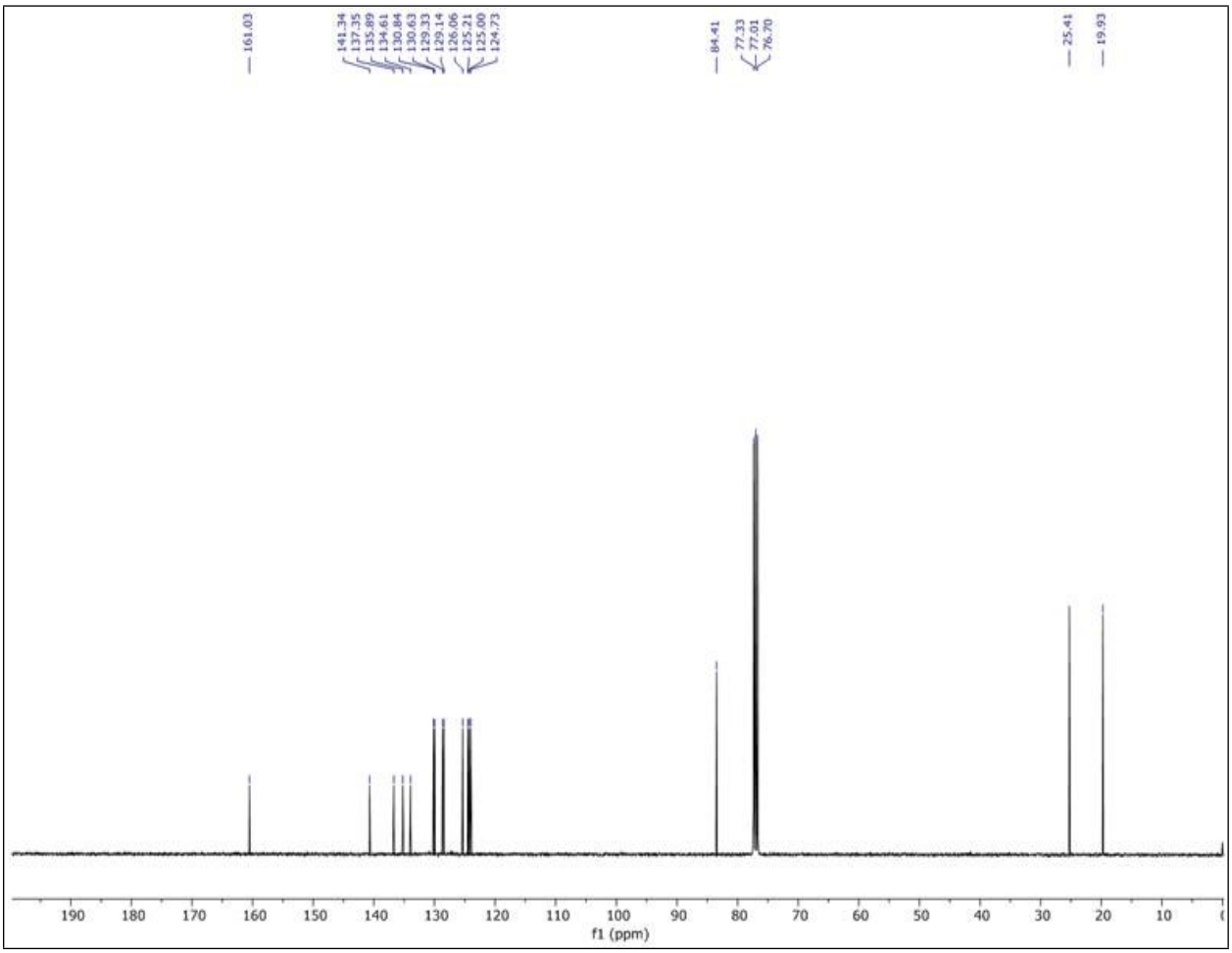

Figure S20. ^{13}C NMR spectra of **3i** in $CDCl_3$.

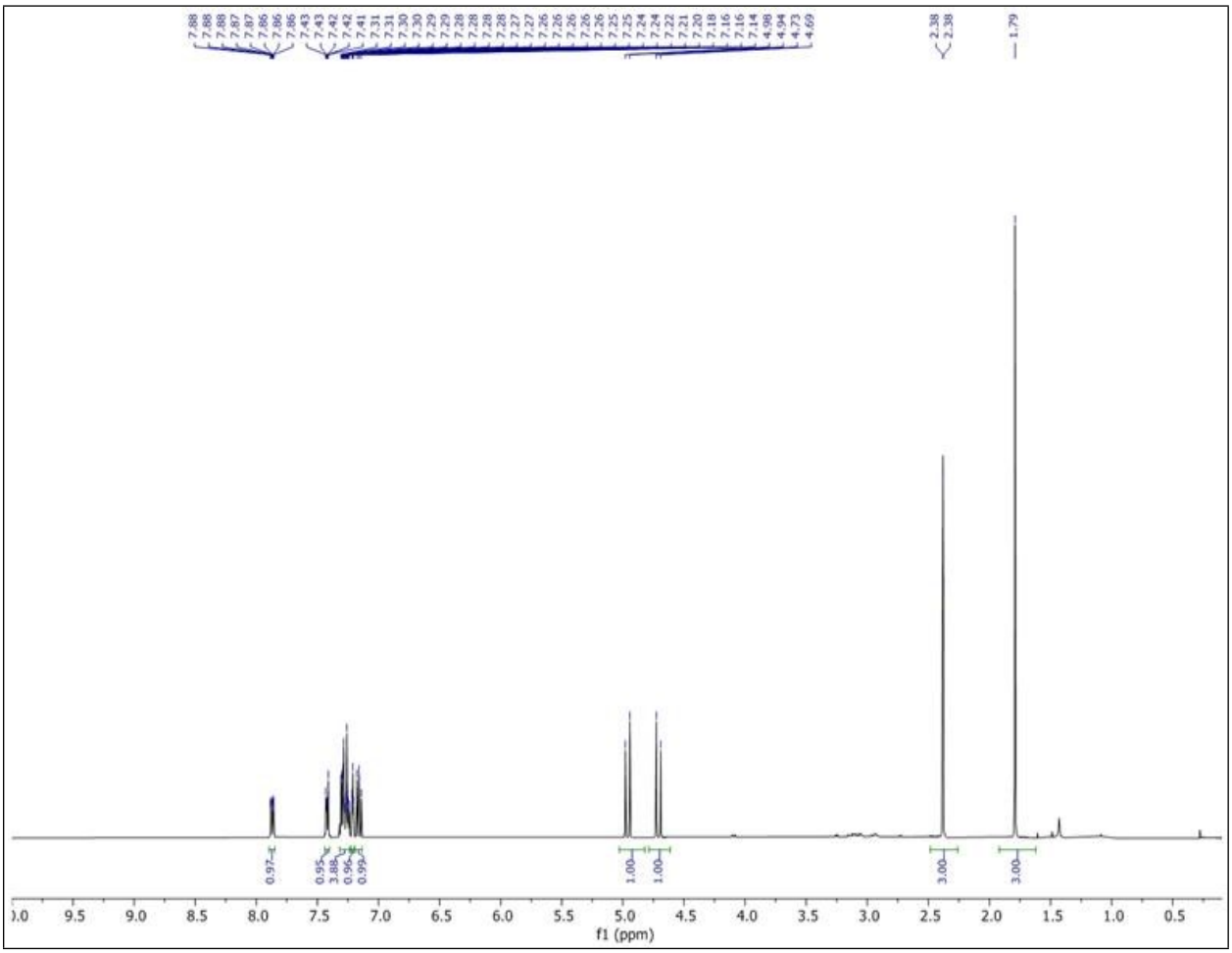

Figure S21. ^{1}H NMR spectra of **3j** in $CDCl_3$.

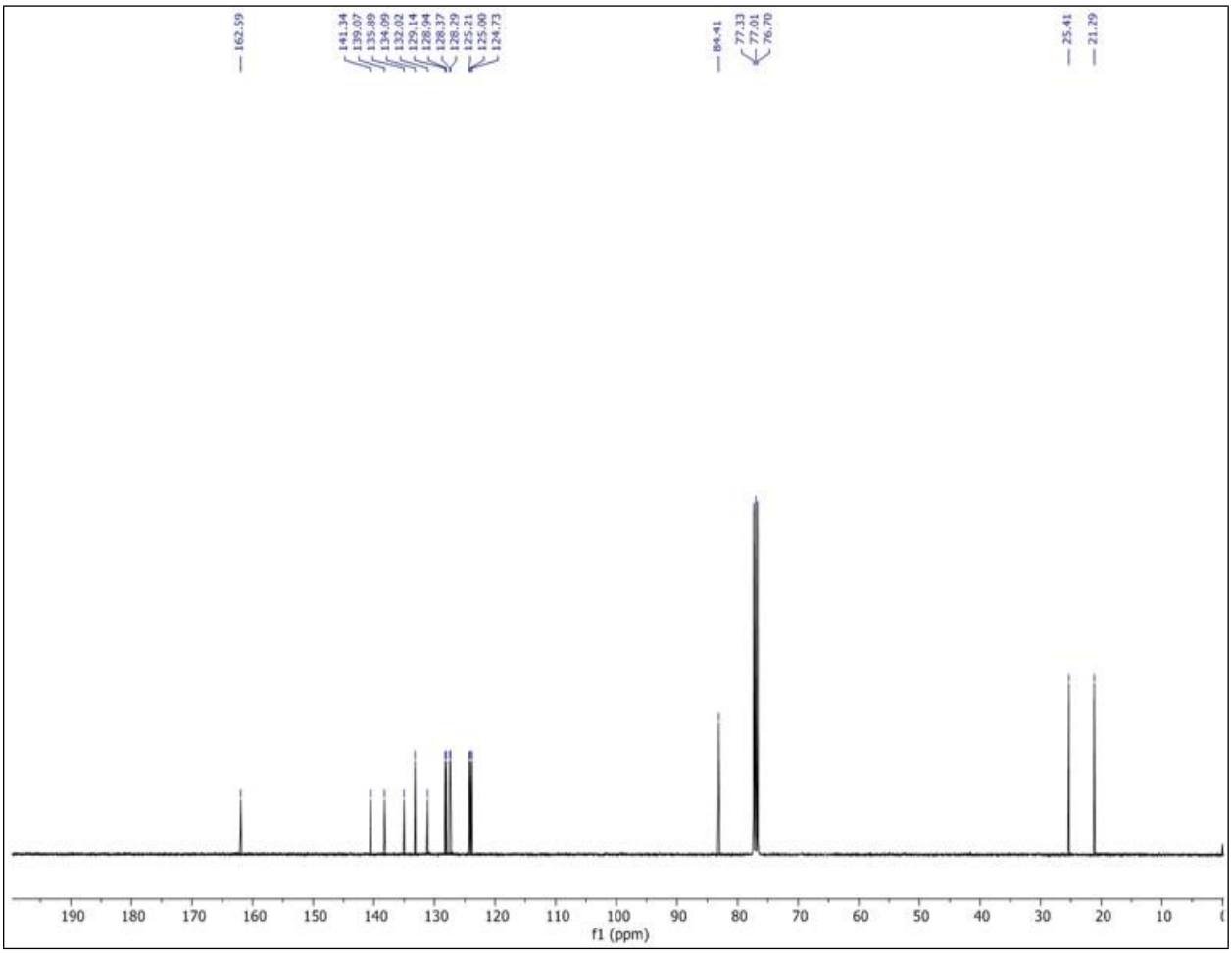

Figure S22. ^{13}C NMR spectra of **3j** in $CDCl_3$.

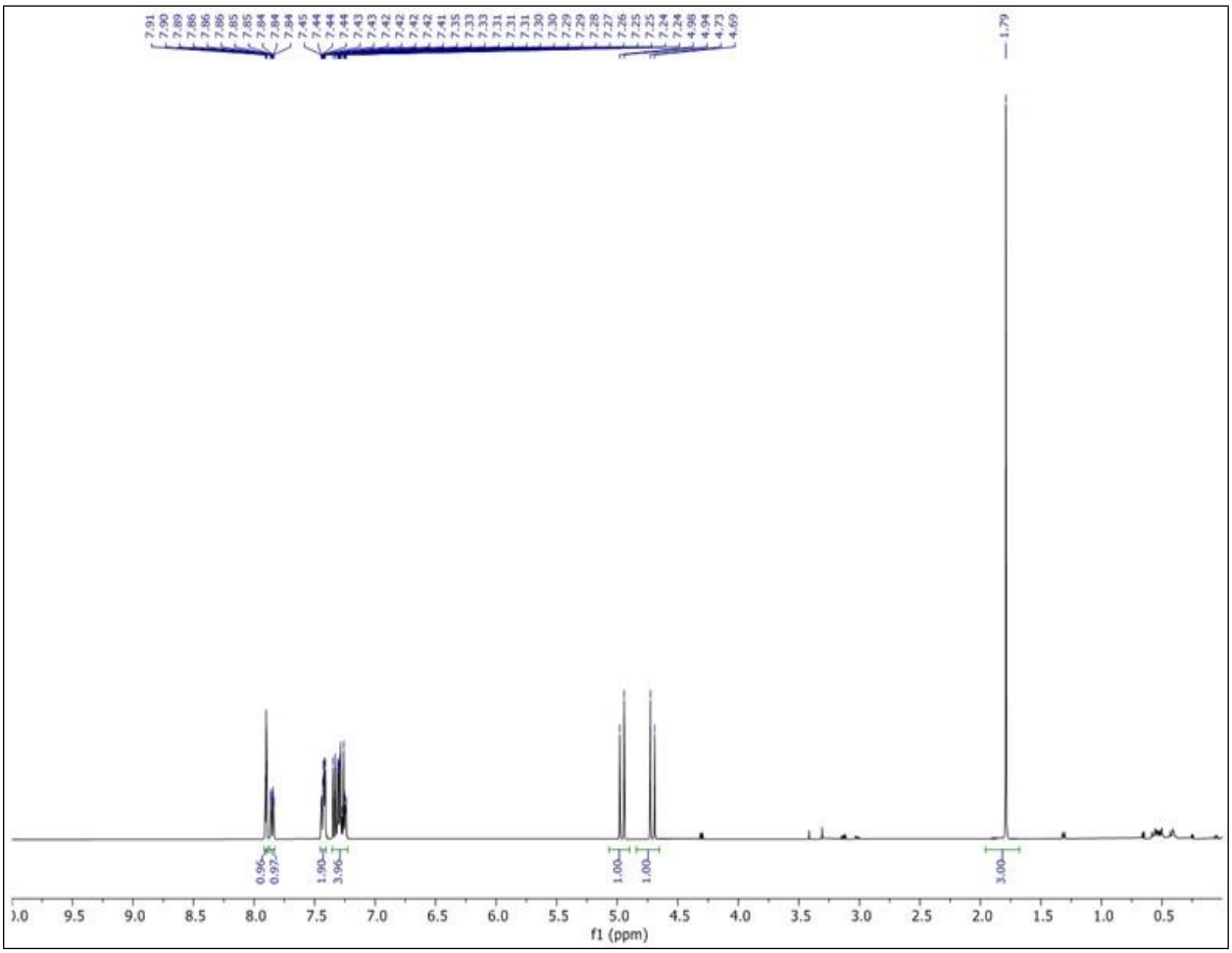

Figure S23. ^{1}H NMR spectra of **3k** in $CDCl_3$.

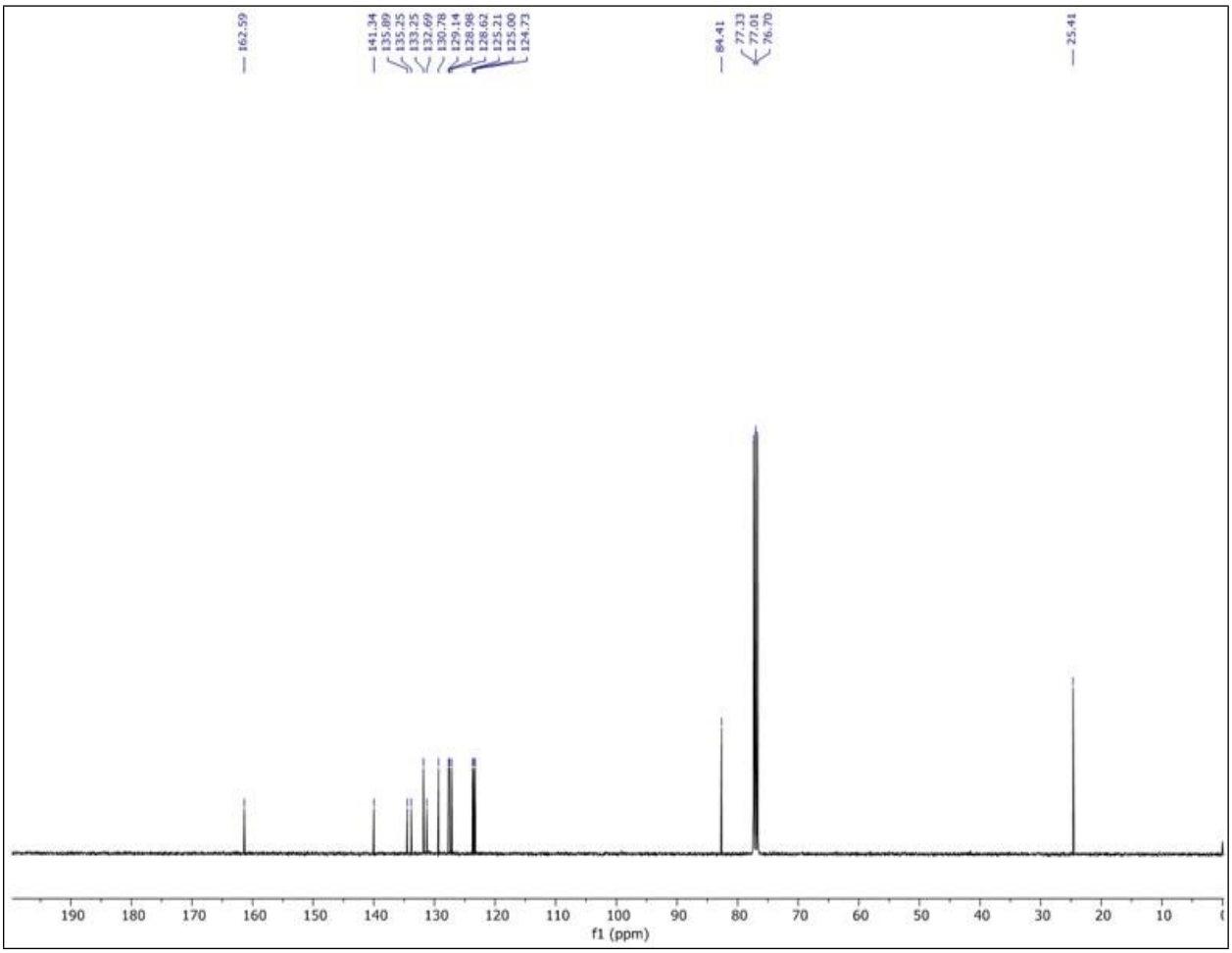

Figure S24. ^{13}C NMR spectra of **3k** in $CDCl_3$.

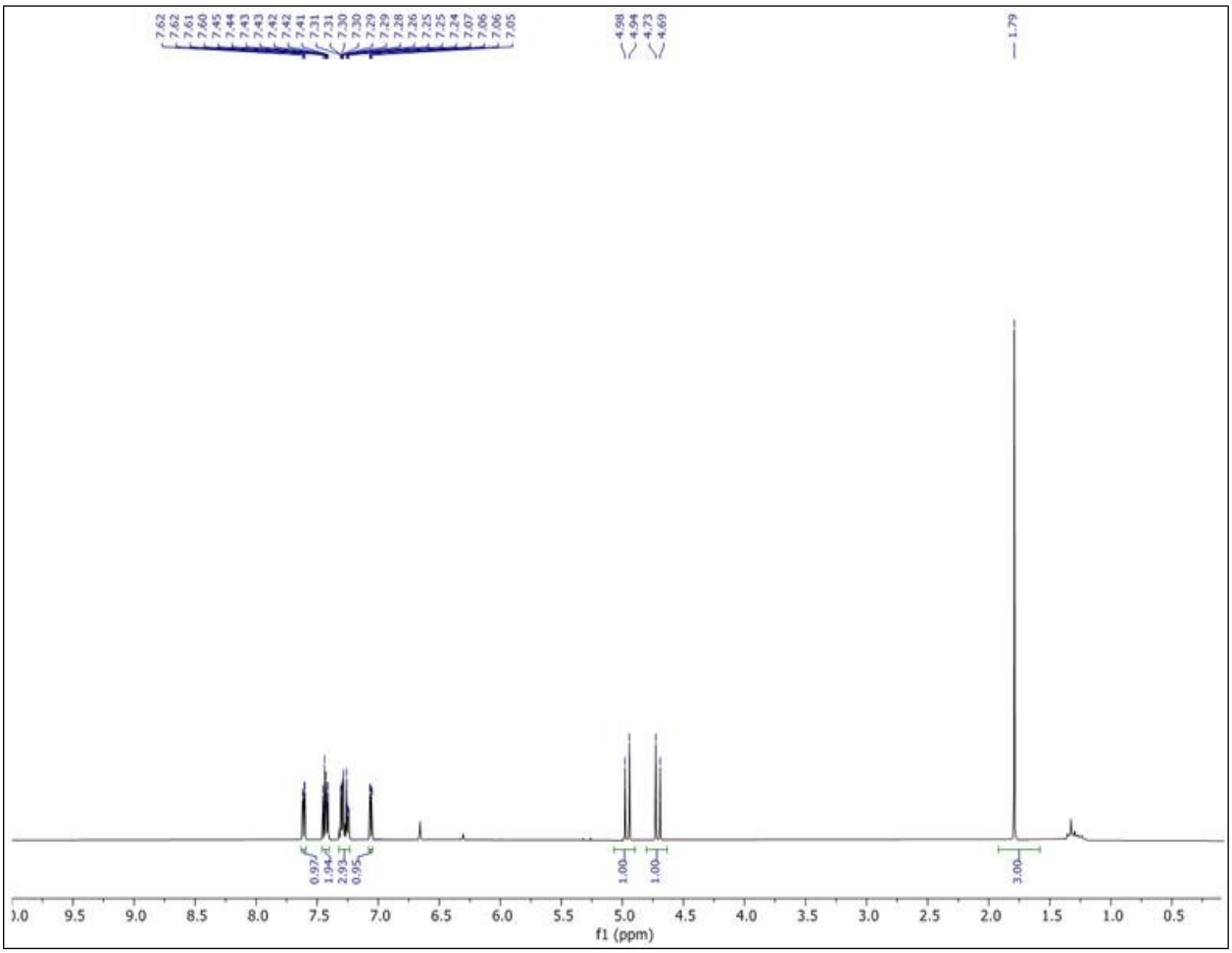

Figure S25. ^{1}H NMR spectra of **3l** in $CDCl_3$.

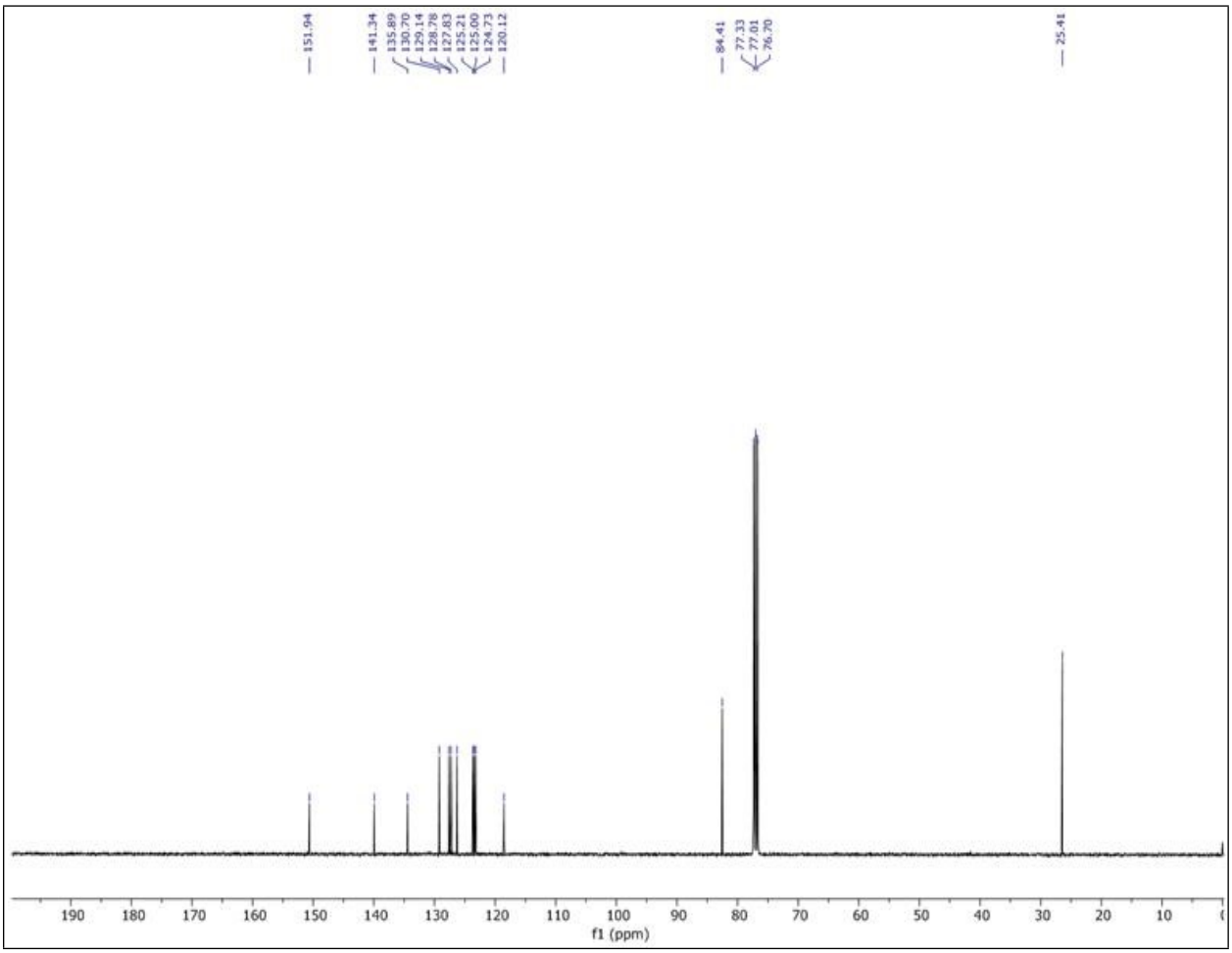

Figure S26. ^{13}C NMR spectra of **3l** in $CDCl_3$.

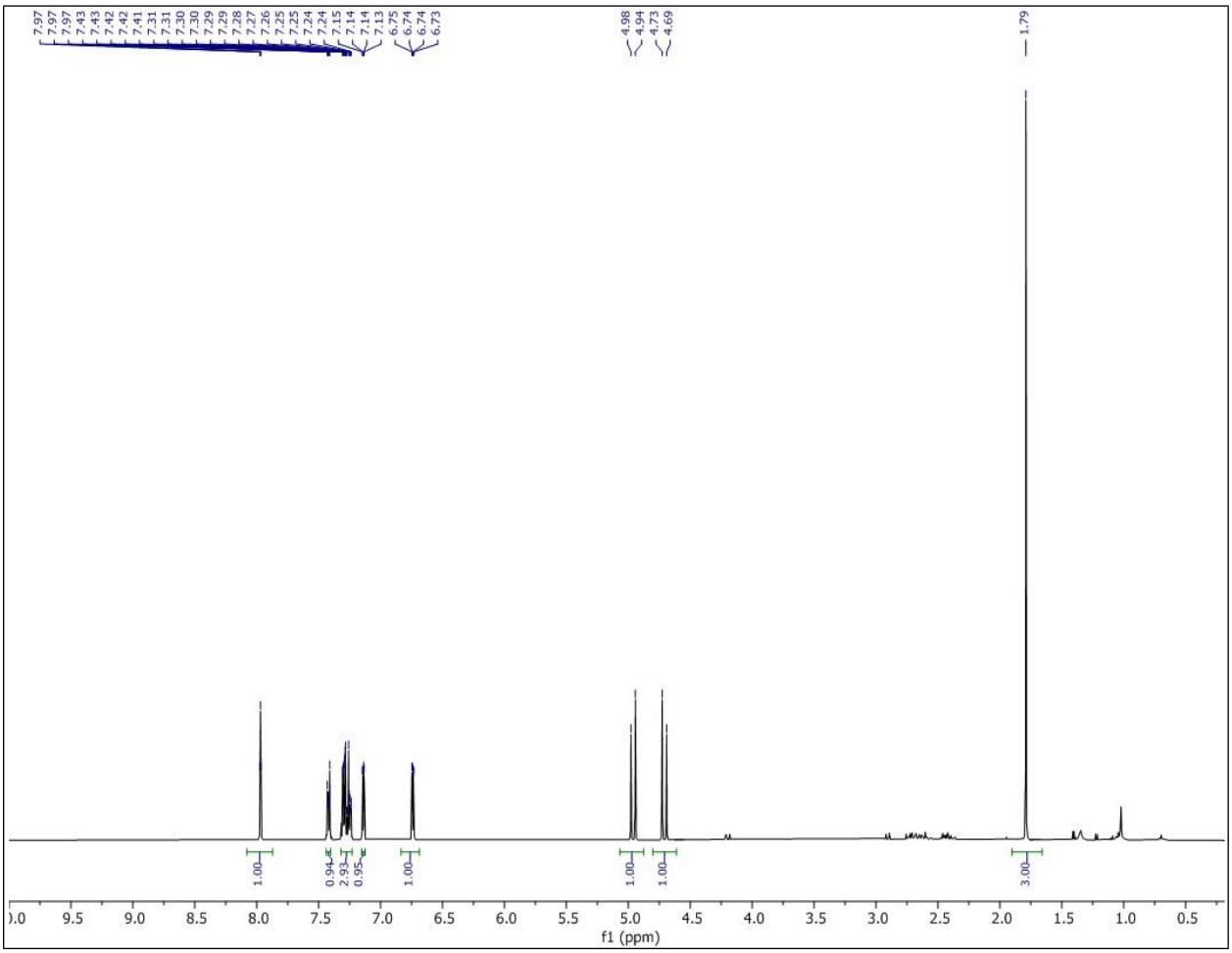

Figure S27. ^{1}H NMR spectra of **3m** in $CDCl_3$.

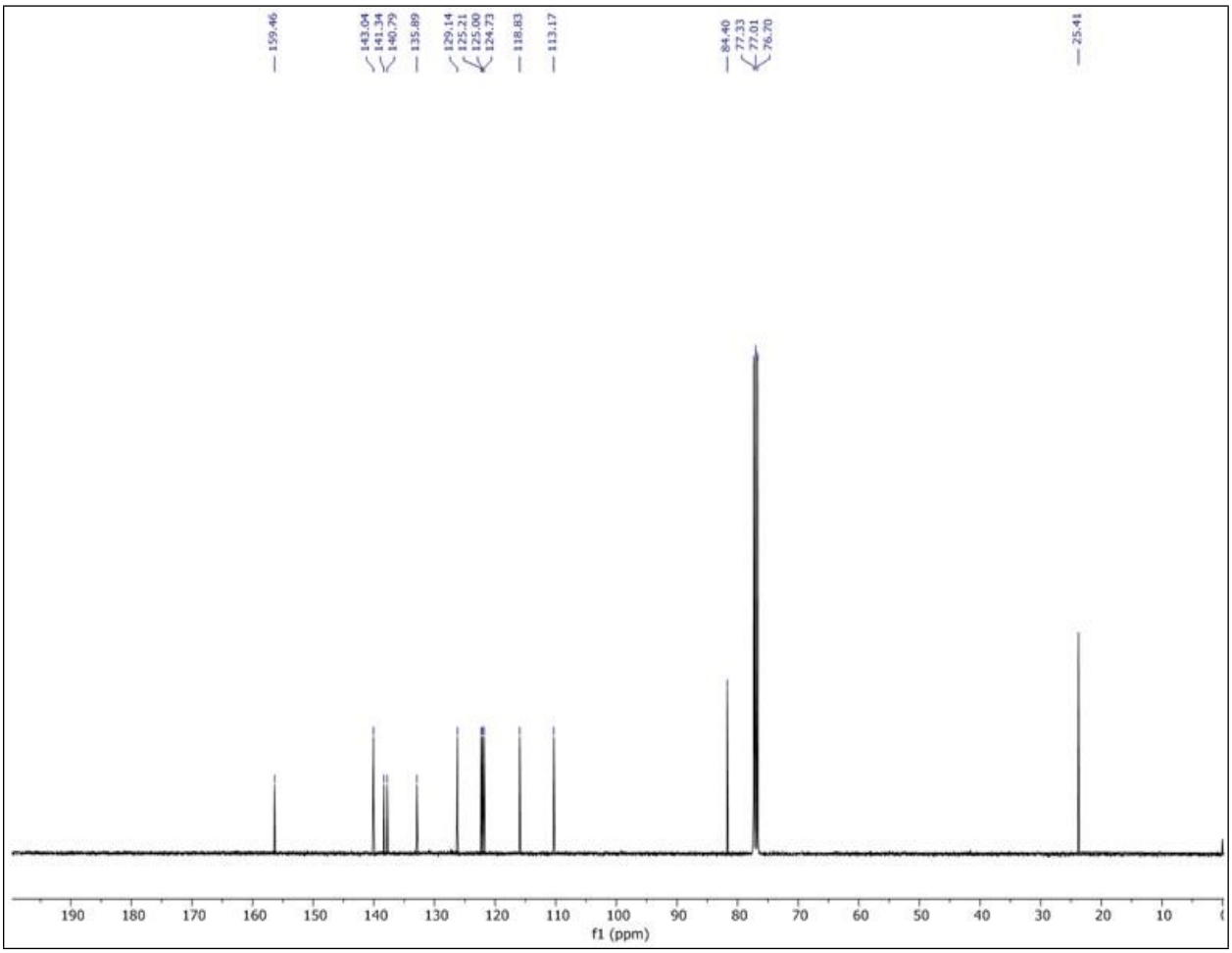

Figure S28. ^{13}C NMR spectra of **3m** in $CDCl_3$.

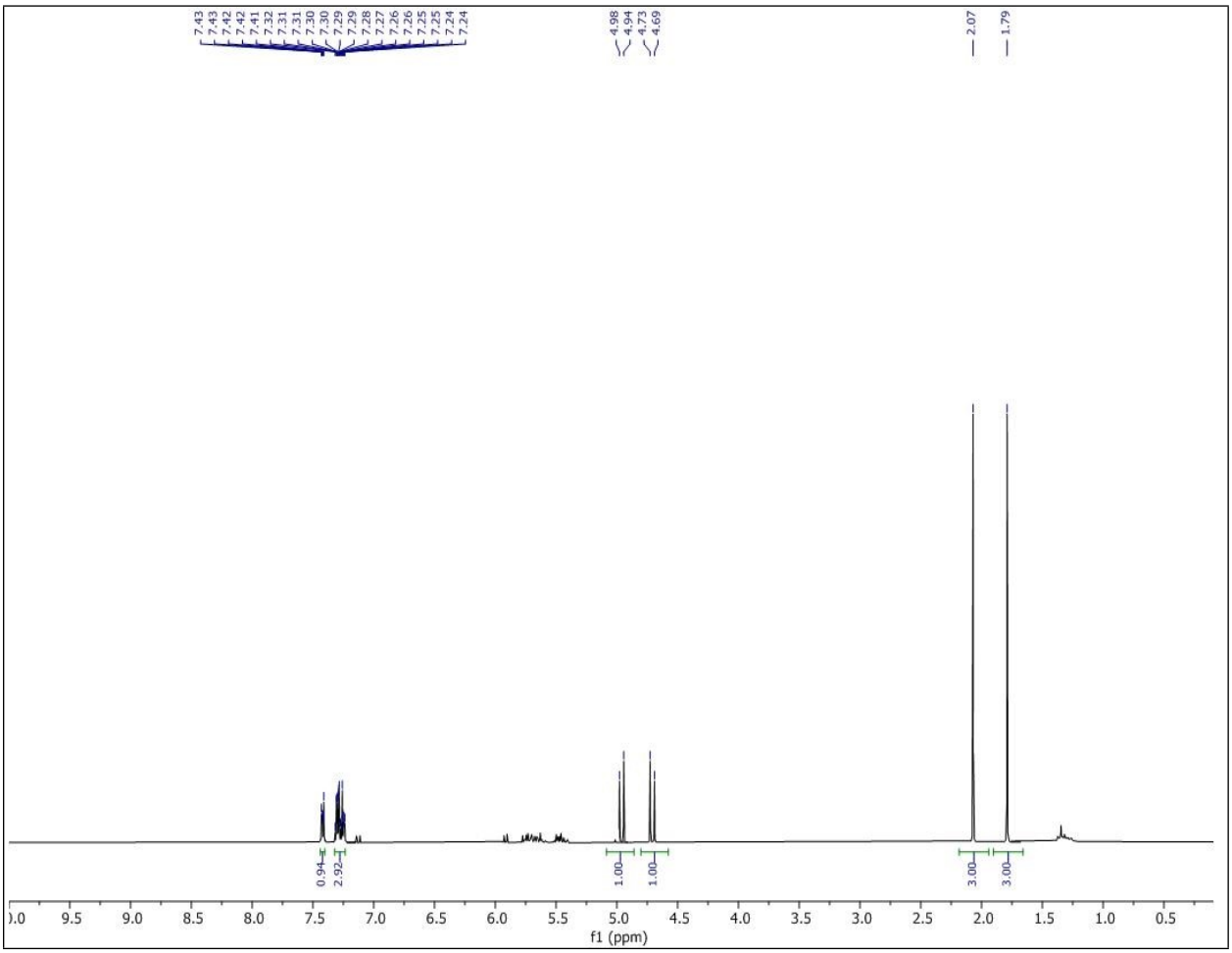

Figure S29. ^{1}H NMR spectra of **3n** in $CDCl_3$.

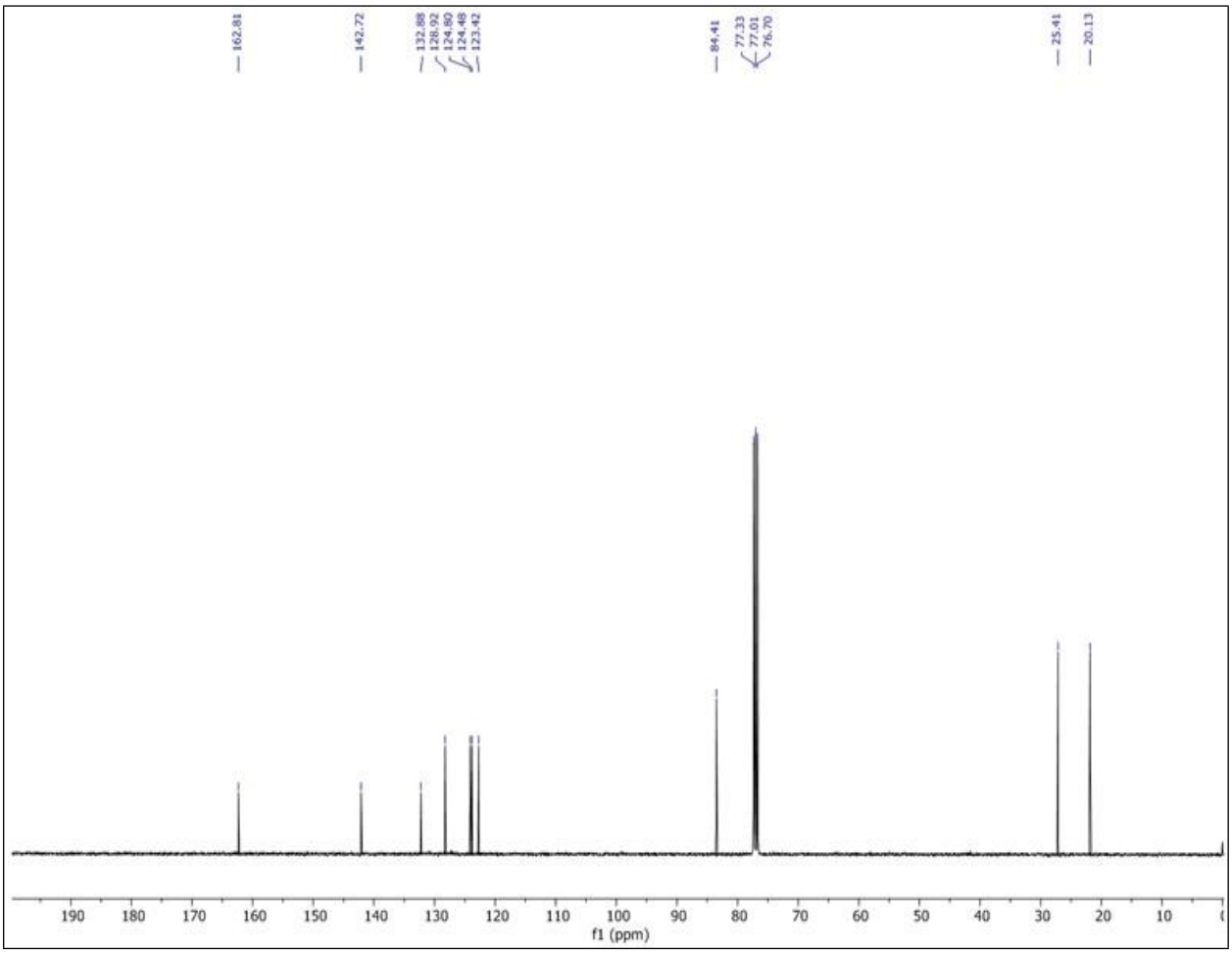

Figure S30. ^{13}C NMR spectra of **3n** in $CDCl_3$.

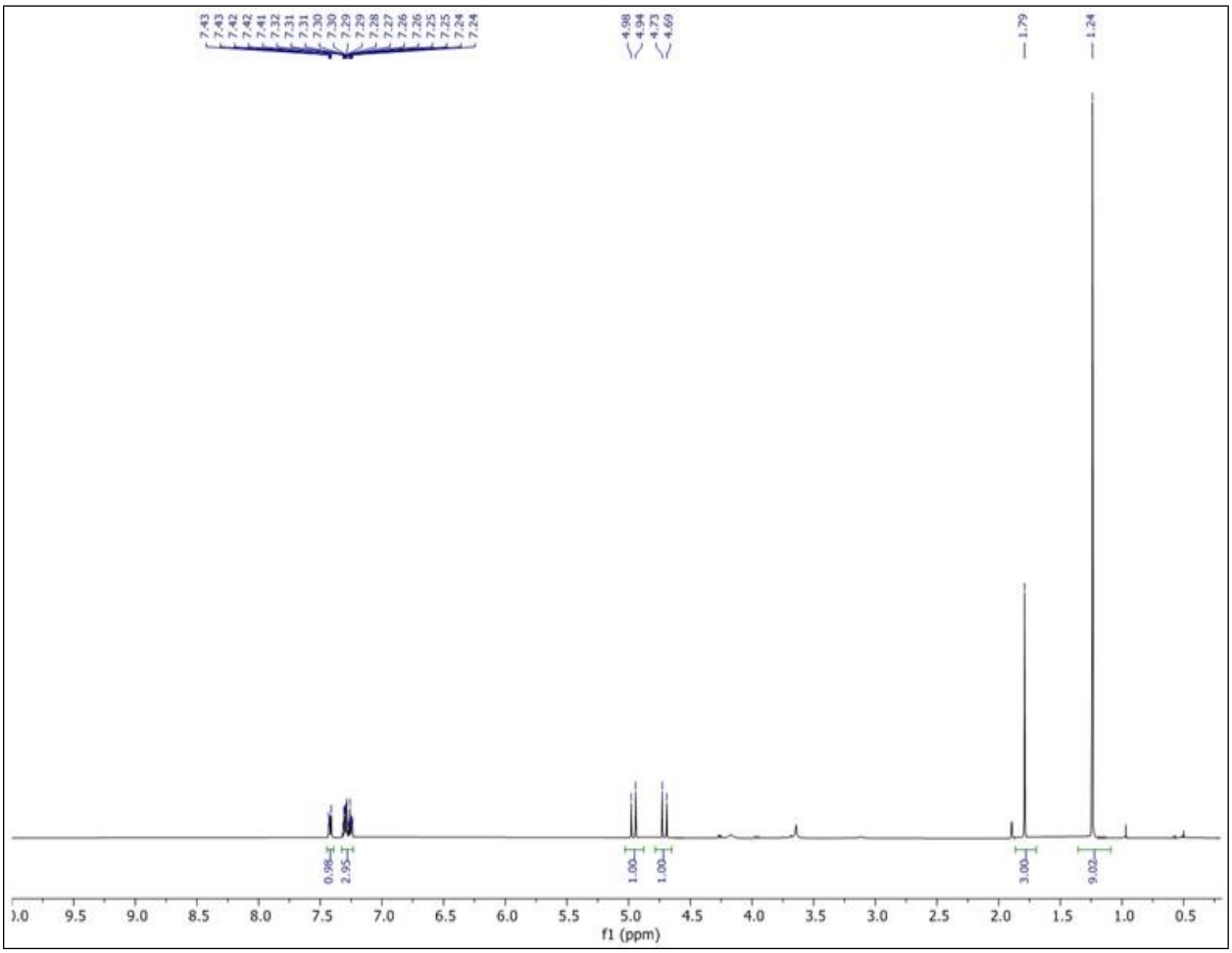

Figure S31. ^{1}H NMR spectra of **3o** in $CDCl_3$.

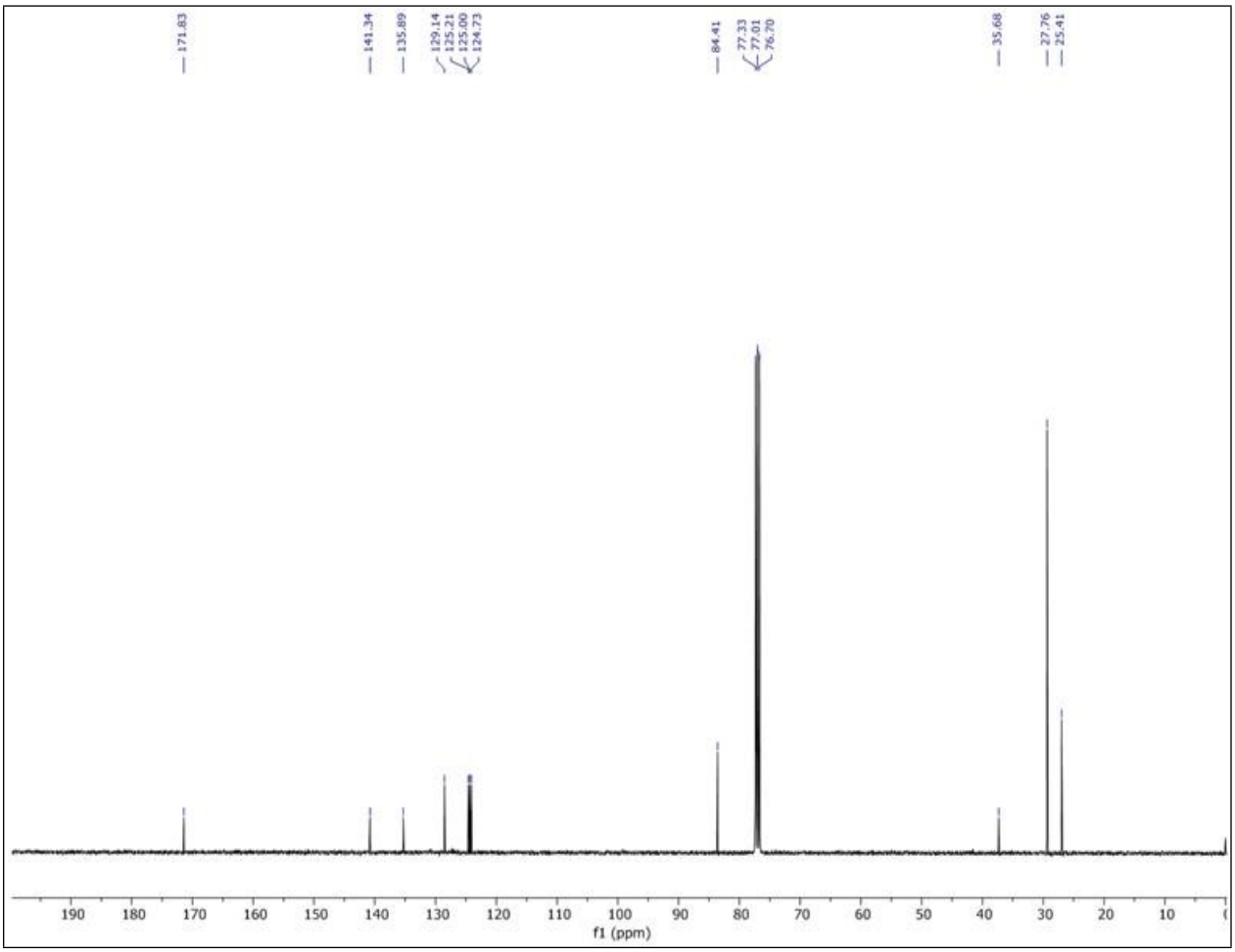

Figure S32. ^{13}C NMR spectra of **3o** in $CDCl_3$.

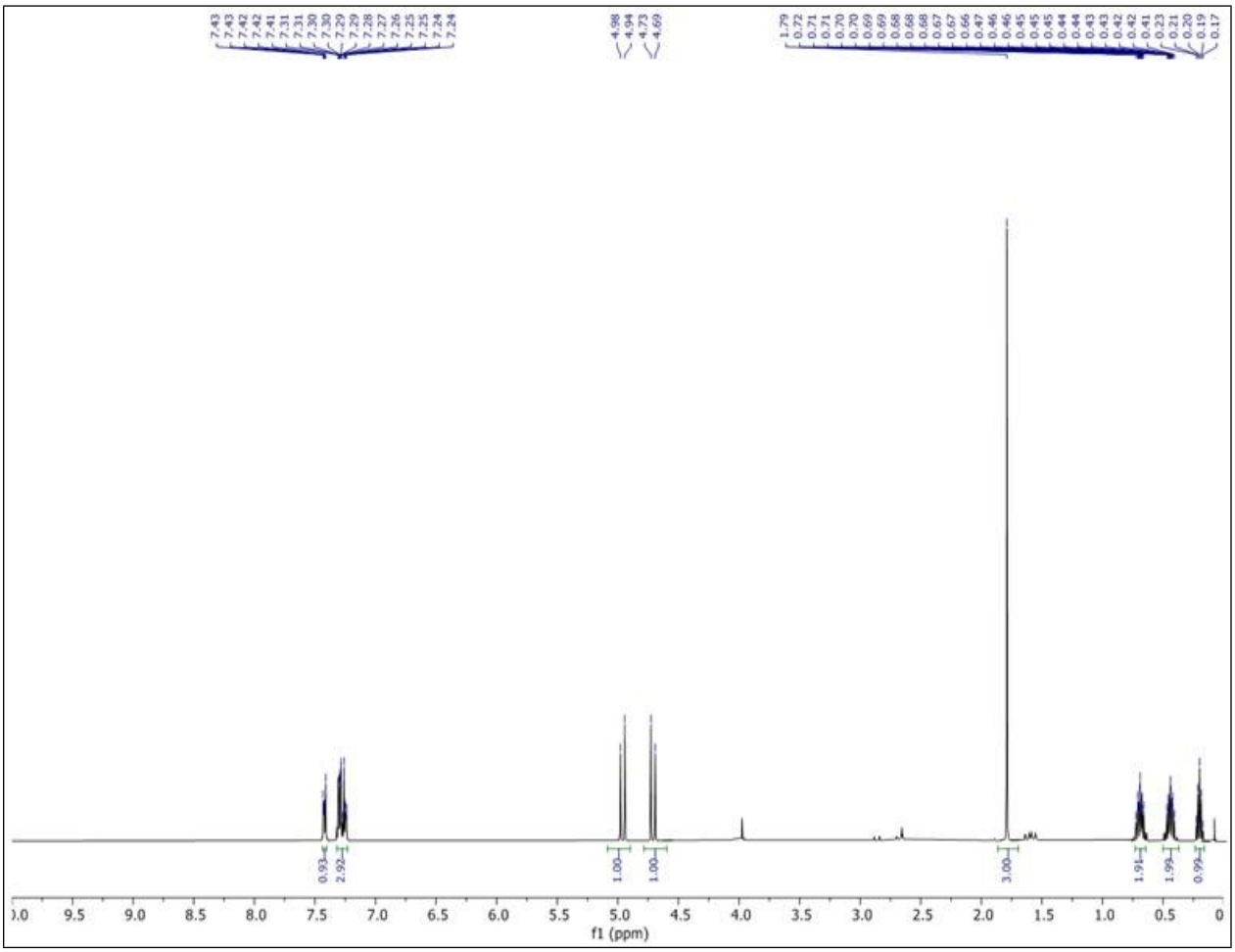

Figure S33. ^{1}H NMR spectra of **3p** in $CDCl_3$.

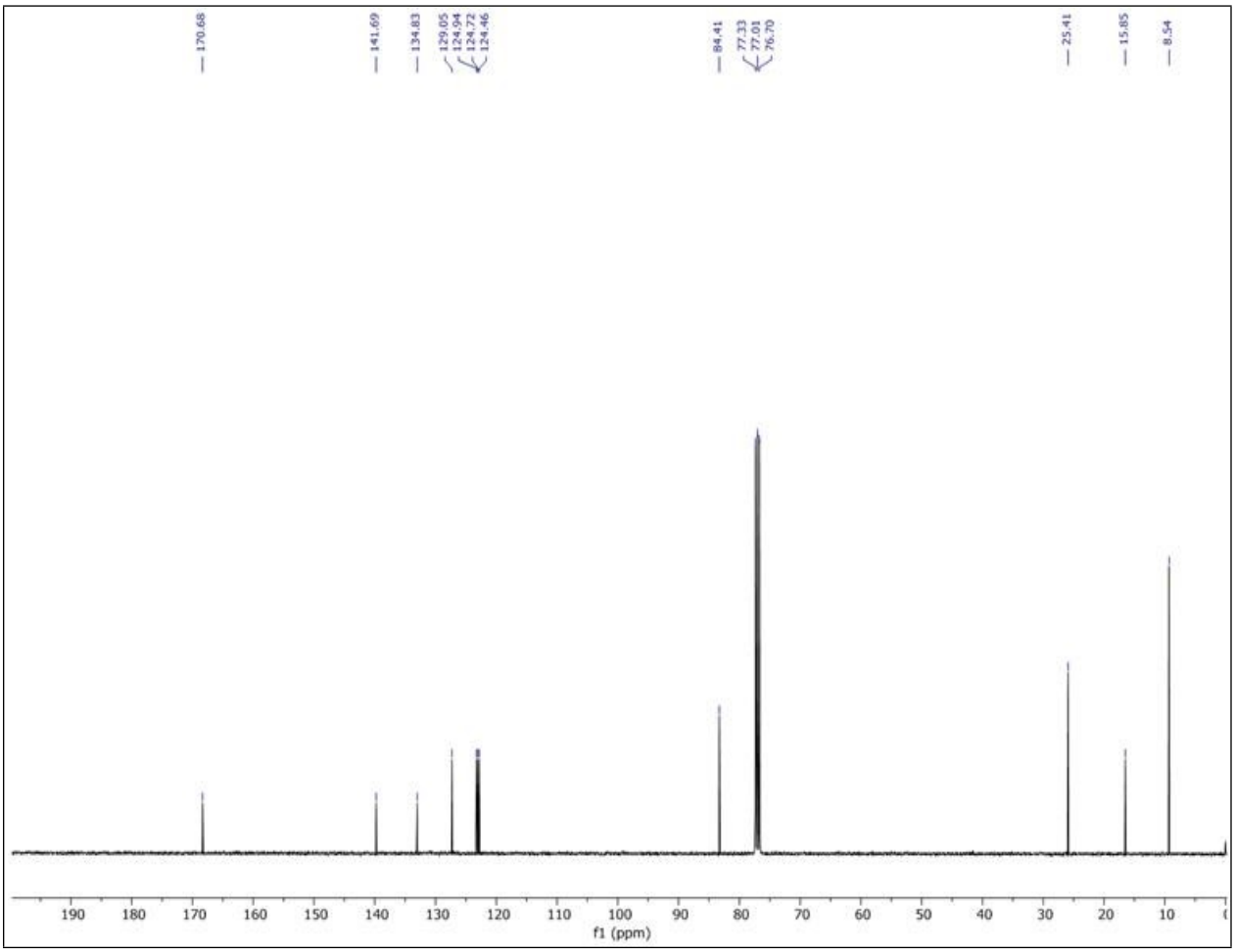

Figure S34. ^{13}C NMR spectra of **3p** in $CDCl_3$.

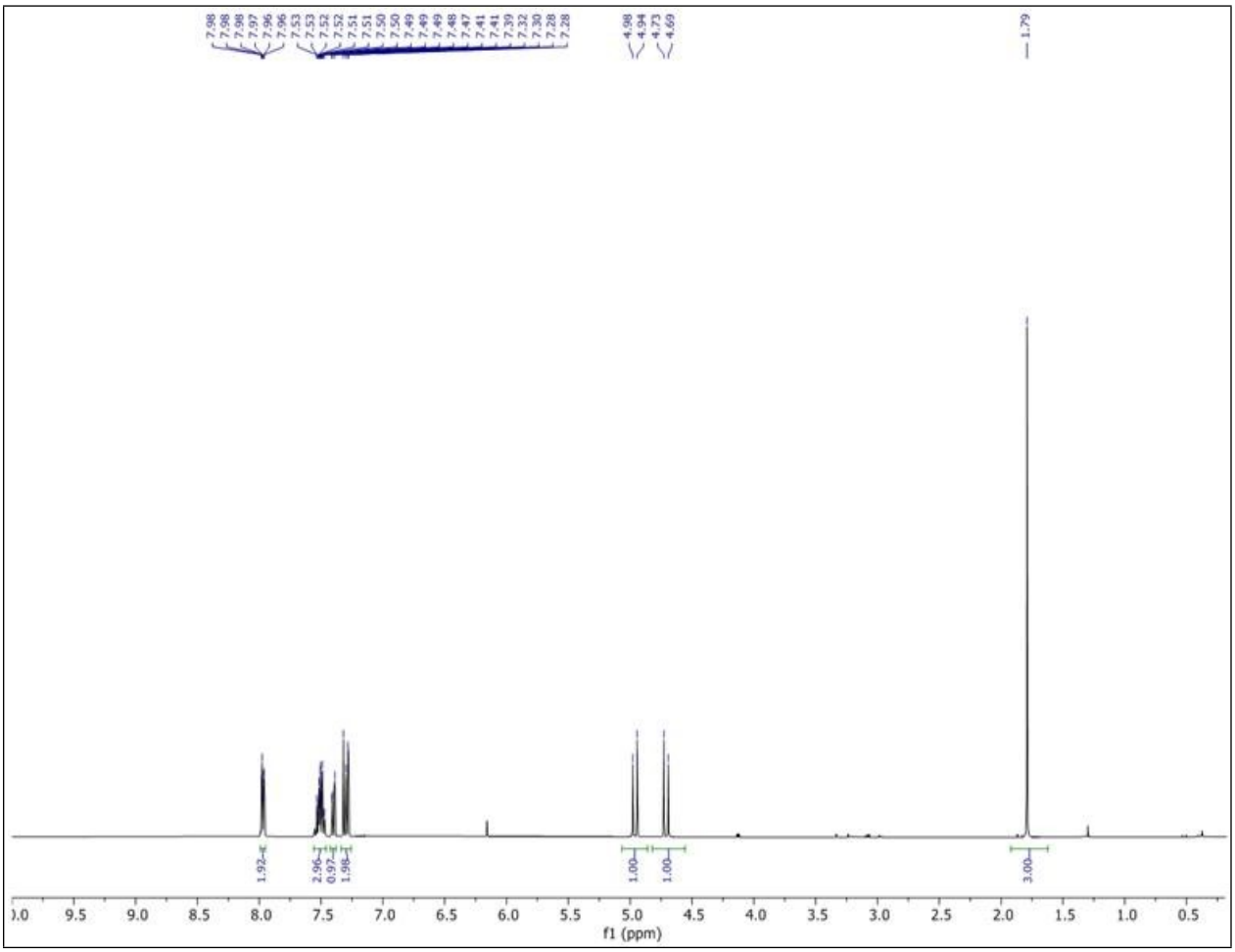

Figure S35. ^{1}H NMR spectra of **3q** in $CDCl_3$.

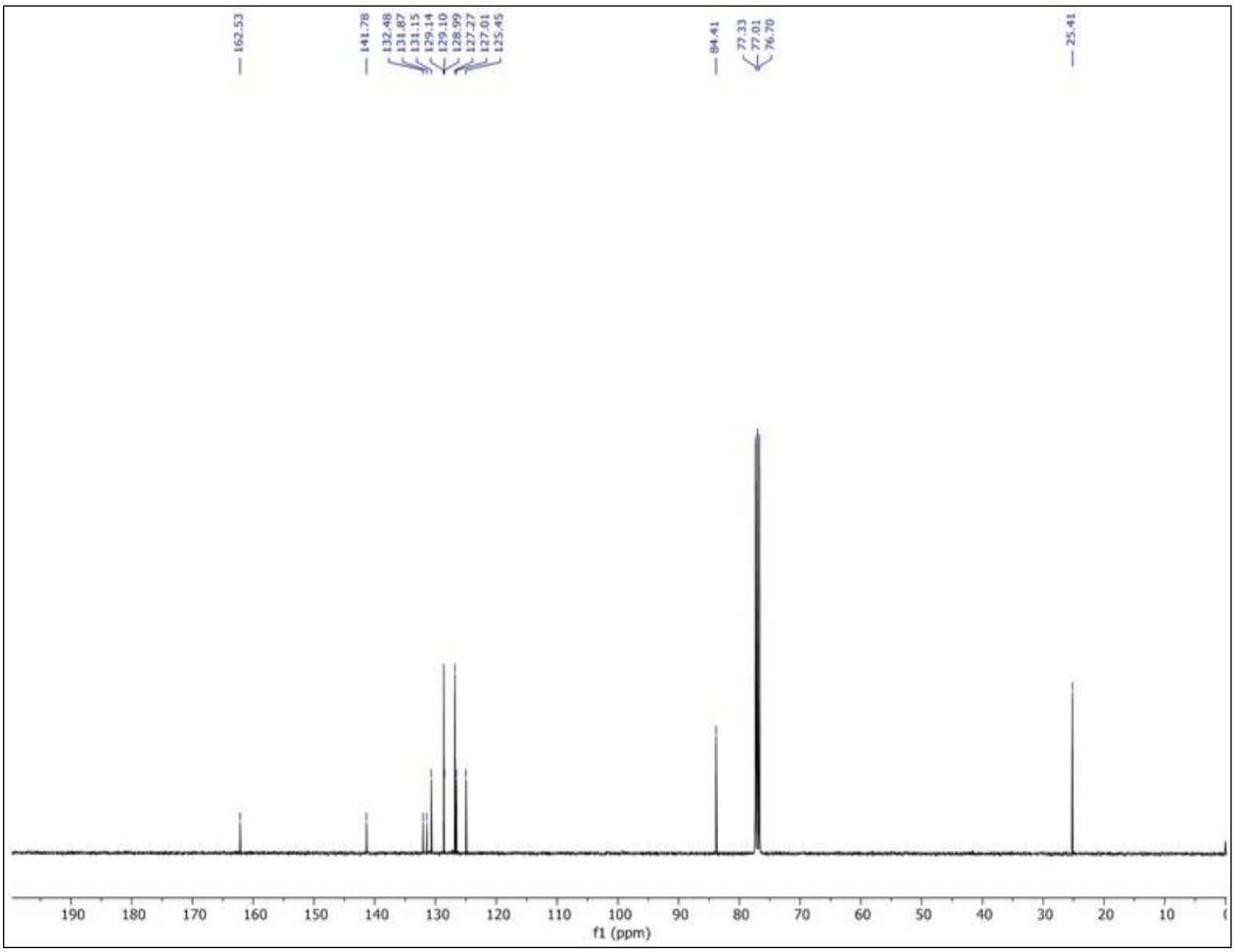

Figure S36. ^{13}C NMR spectra of **3q** in $CDCl_3$.

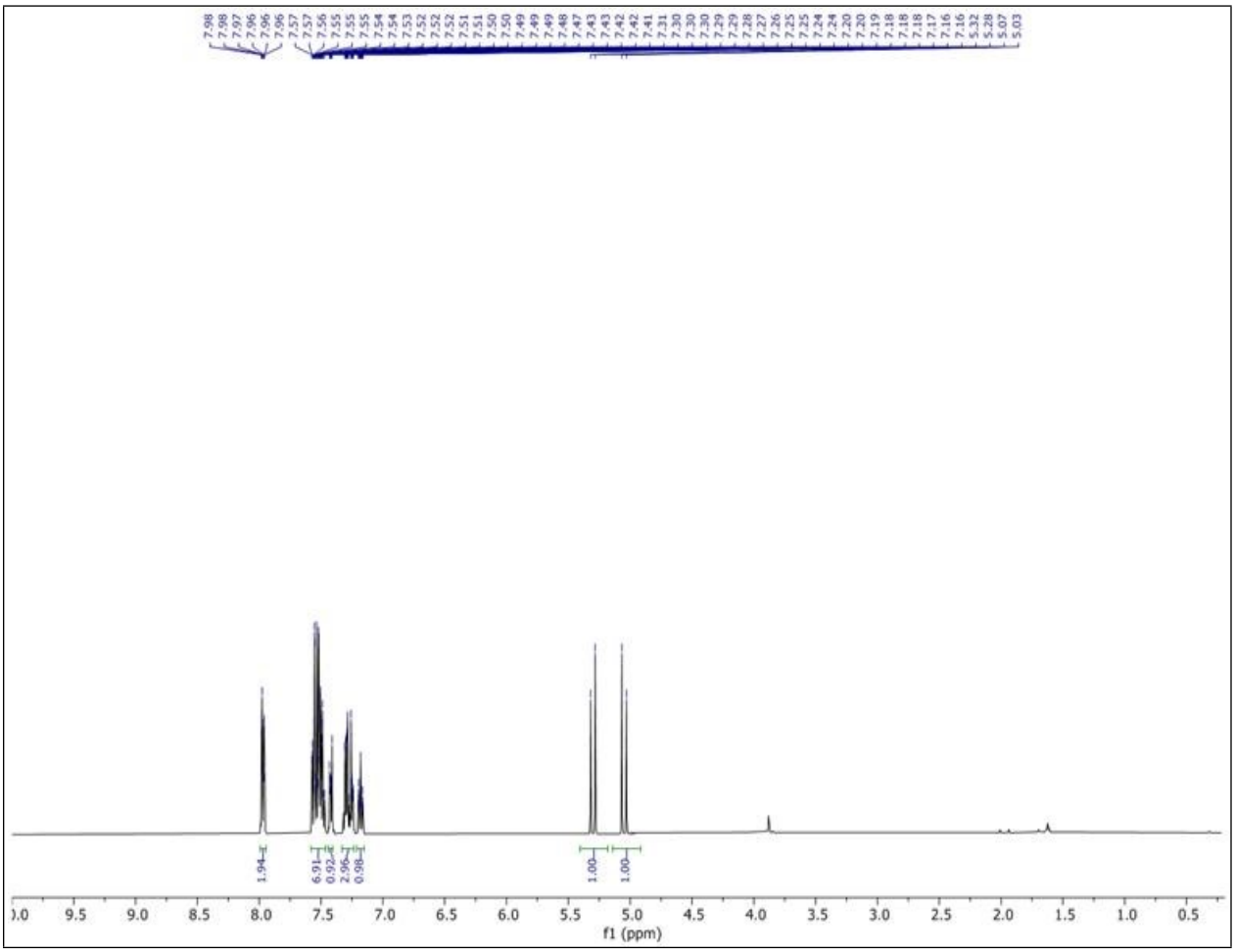

Figure S37. ^{1}H NMR spectra of **3r** in $CDCl_3$.

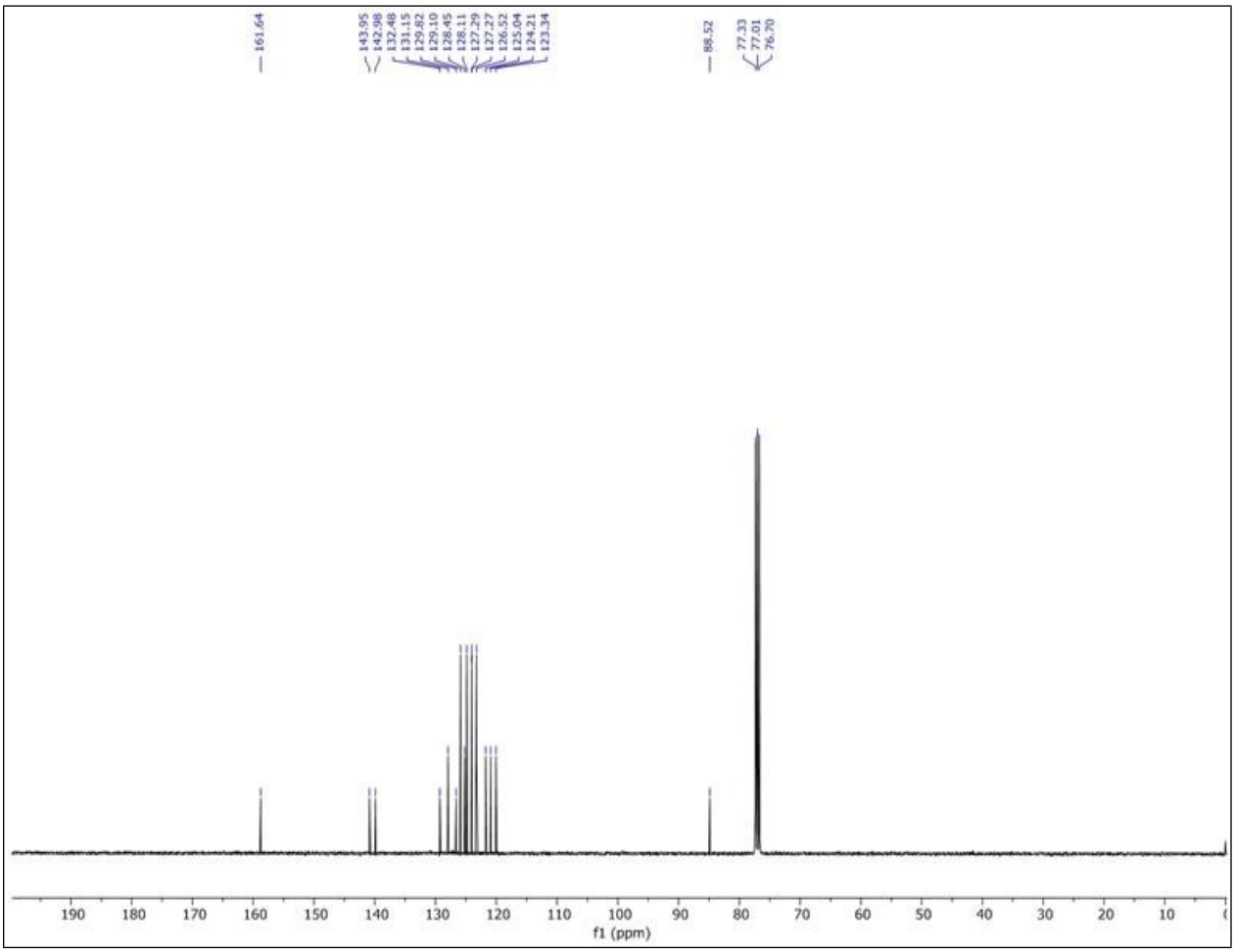

Figure S38. ^{13}C NMR spectra of **3r** in $CDCl_3$.

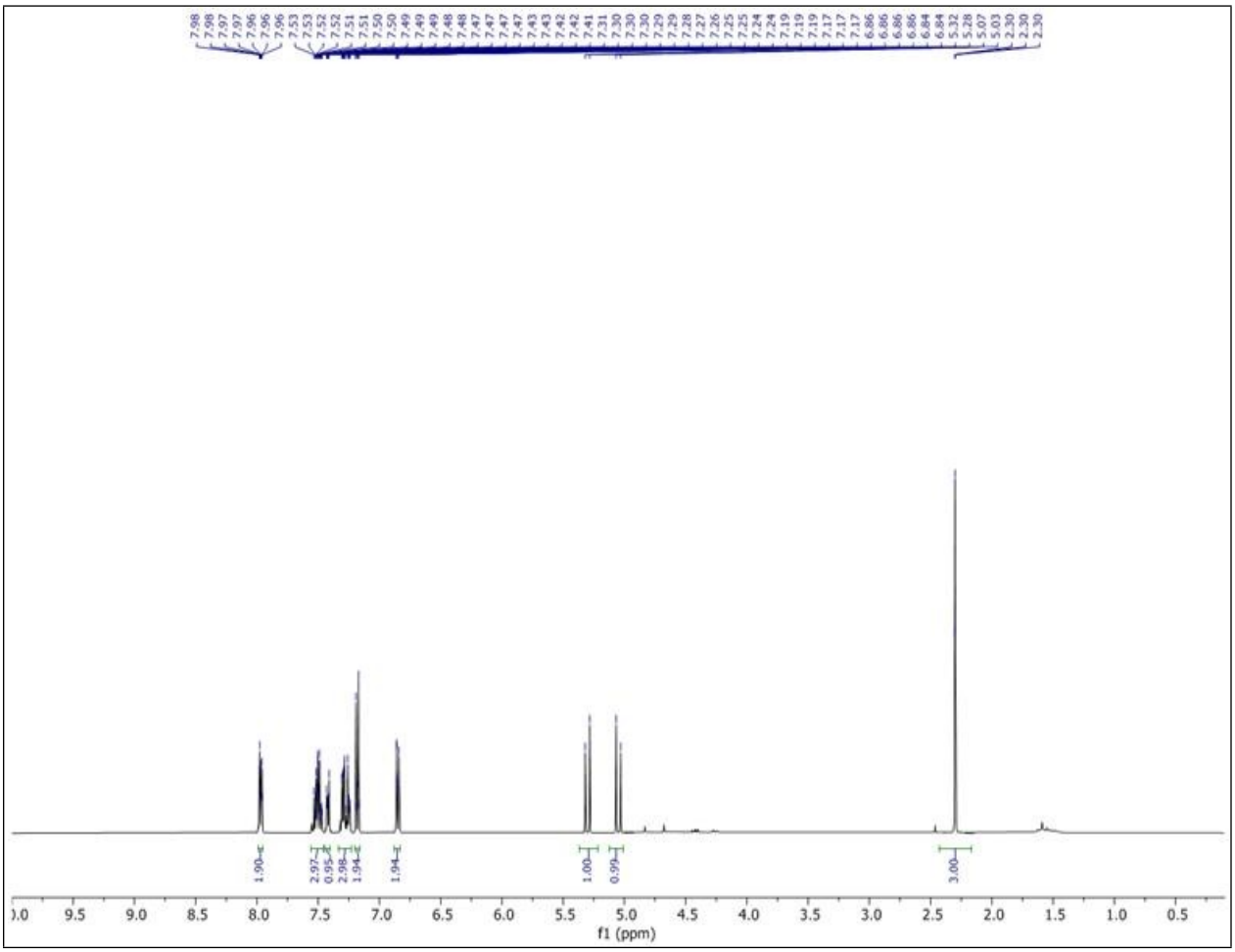

Figure S39. ^{1}H NMR spectra of **3s** in $CDCl_3$.

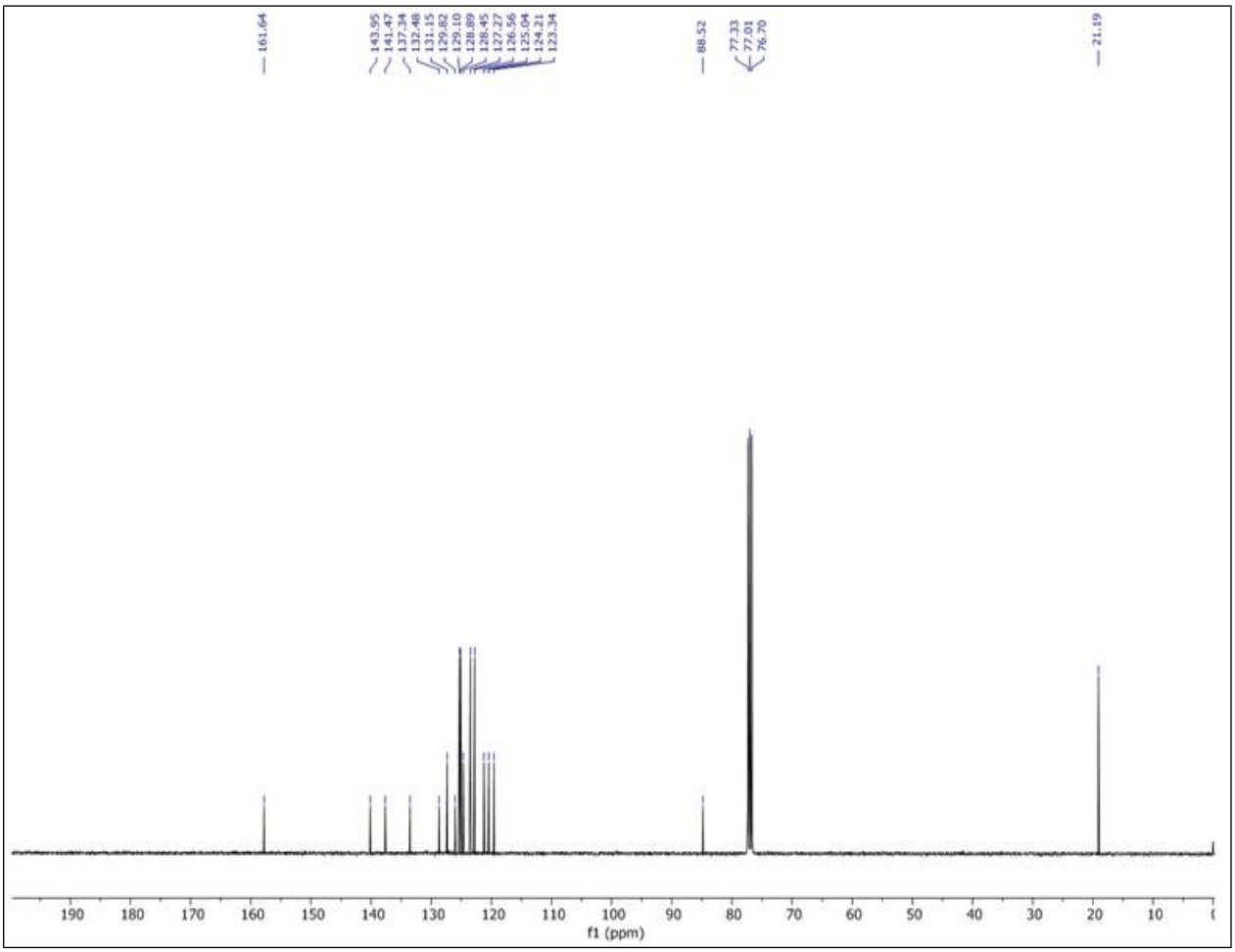

Figure S40. ^{13}C NMR spectra of **3s** in $CDCl_3$.

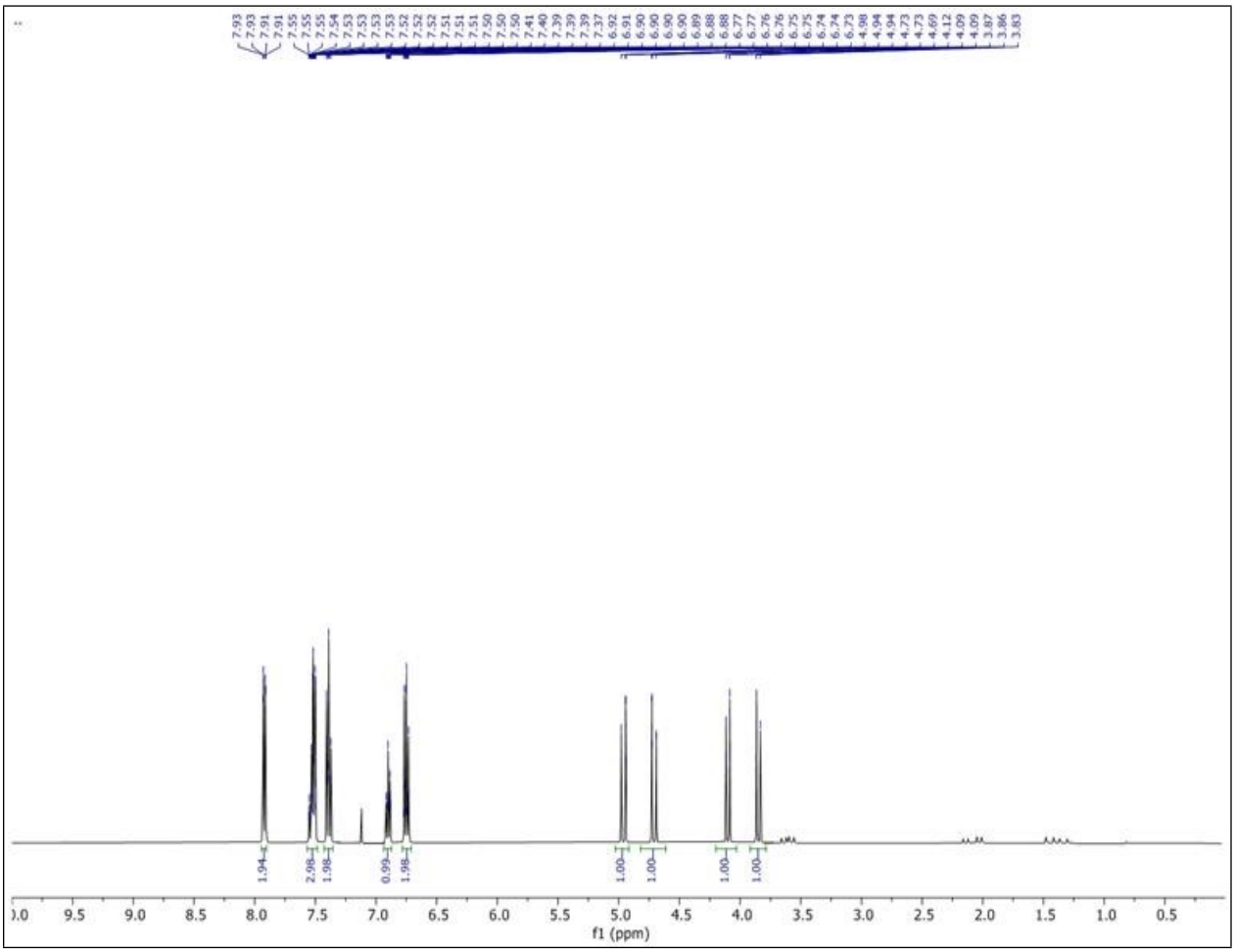

Figure S41. ^{1}H NMR spectra of **5a** in $CDCl_3$.

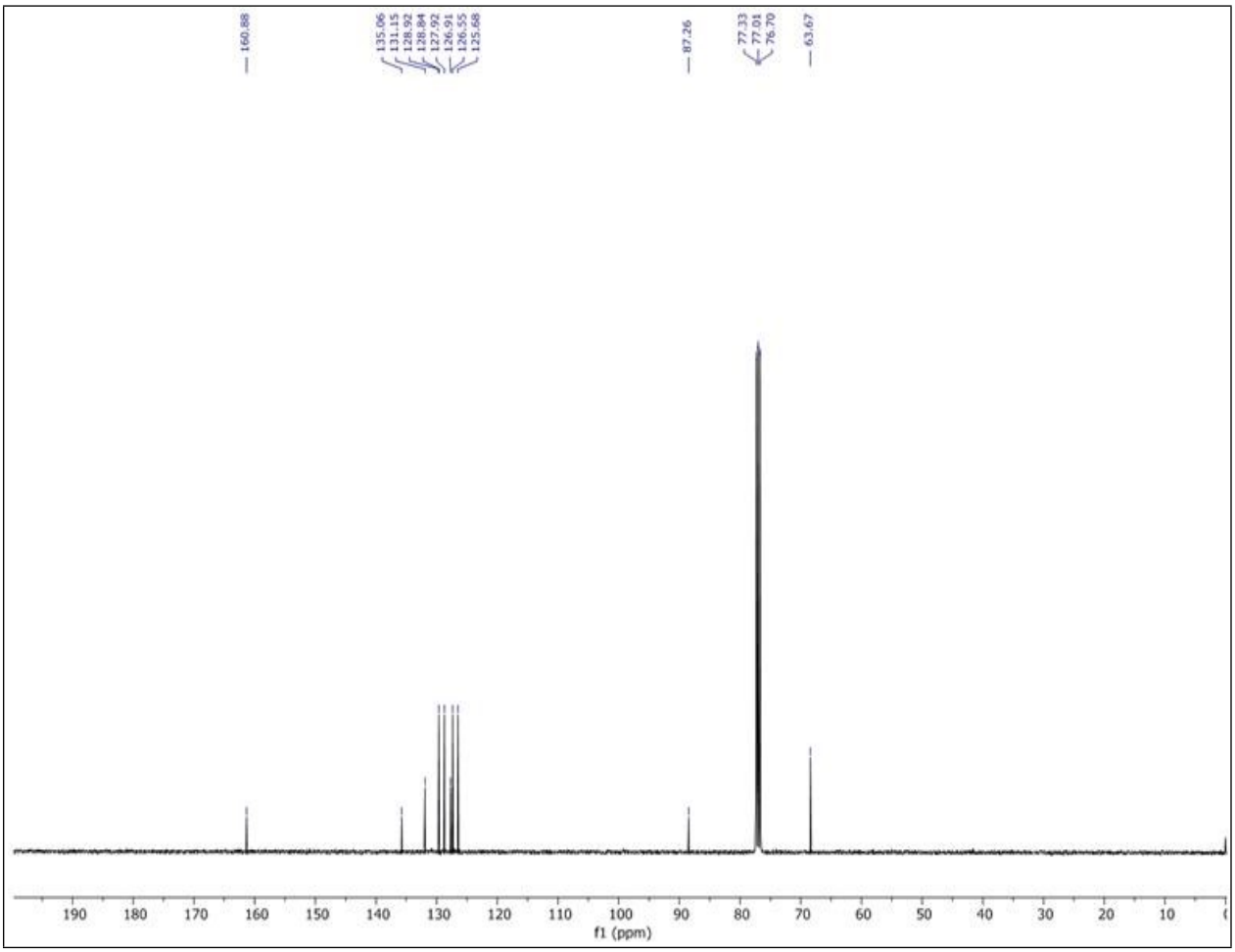

Figure S42. ^{13}C NMR spectra of **5a** in $CDCl_3$.

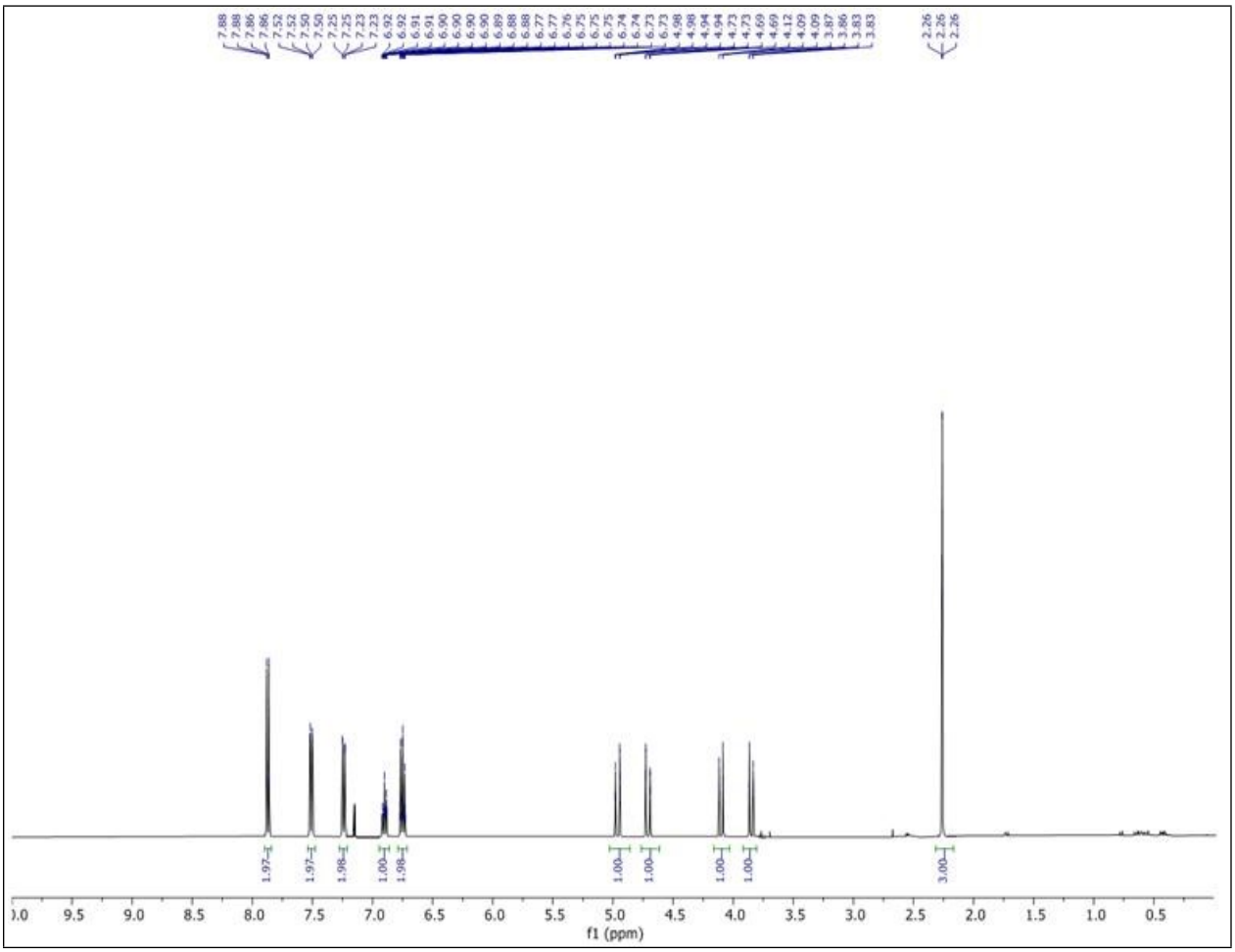

Figure S43. ^{1}H NMR spectra of **5b** in $CDCl_3$.

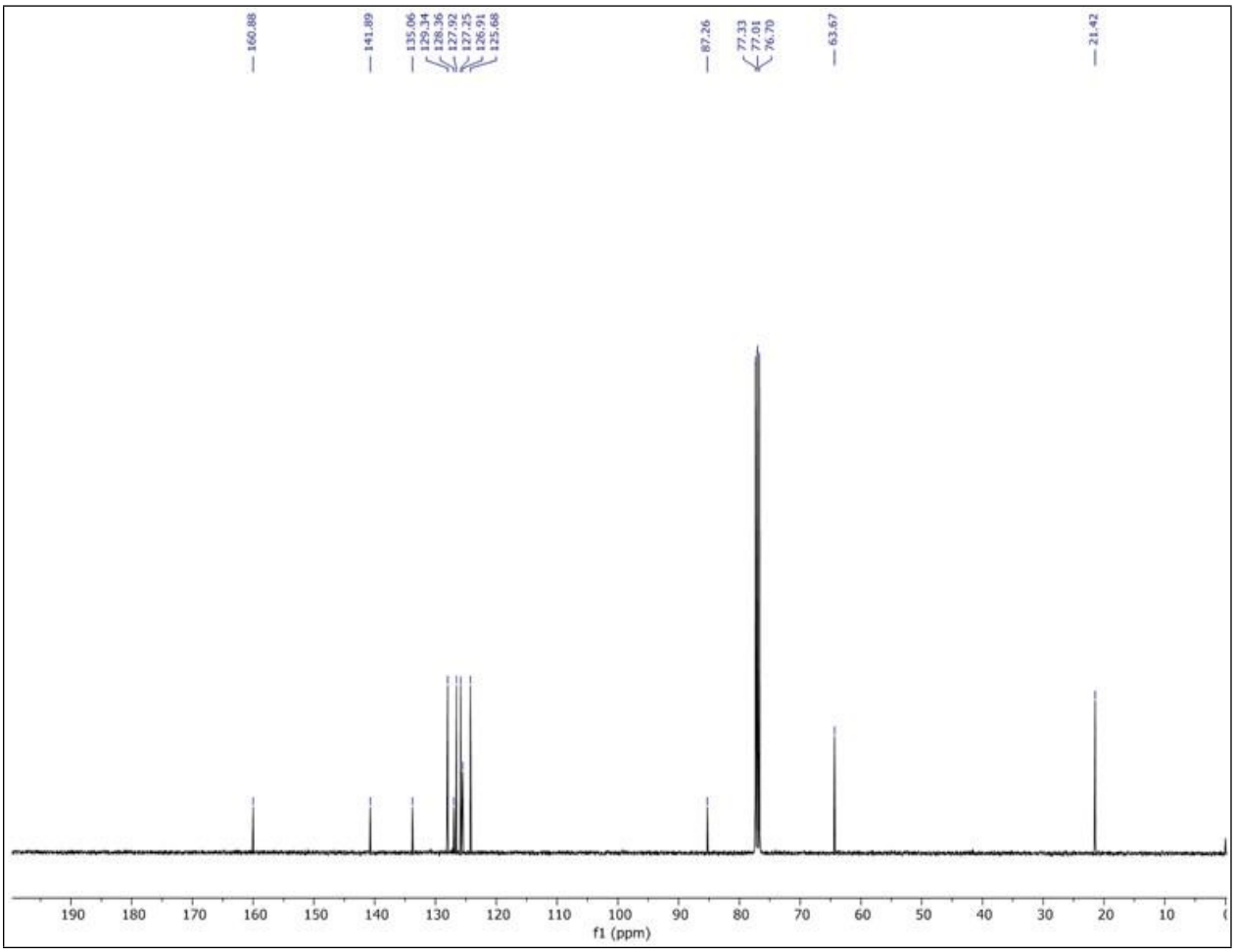

Figure S44. ^{13}C NMR spectra of **5b** in $CDCl_3$.

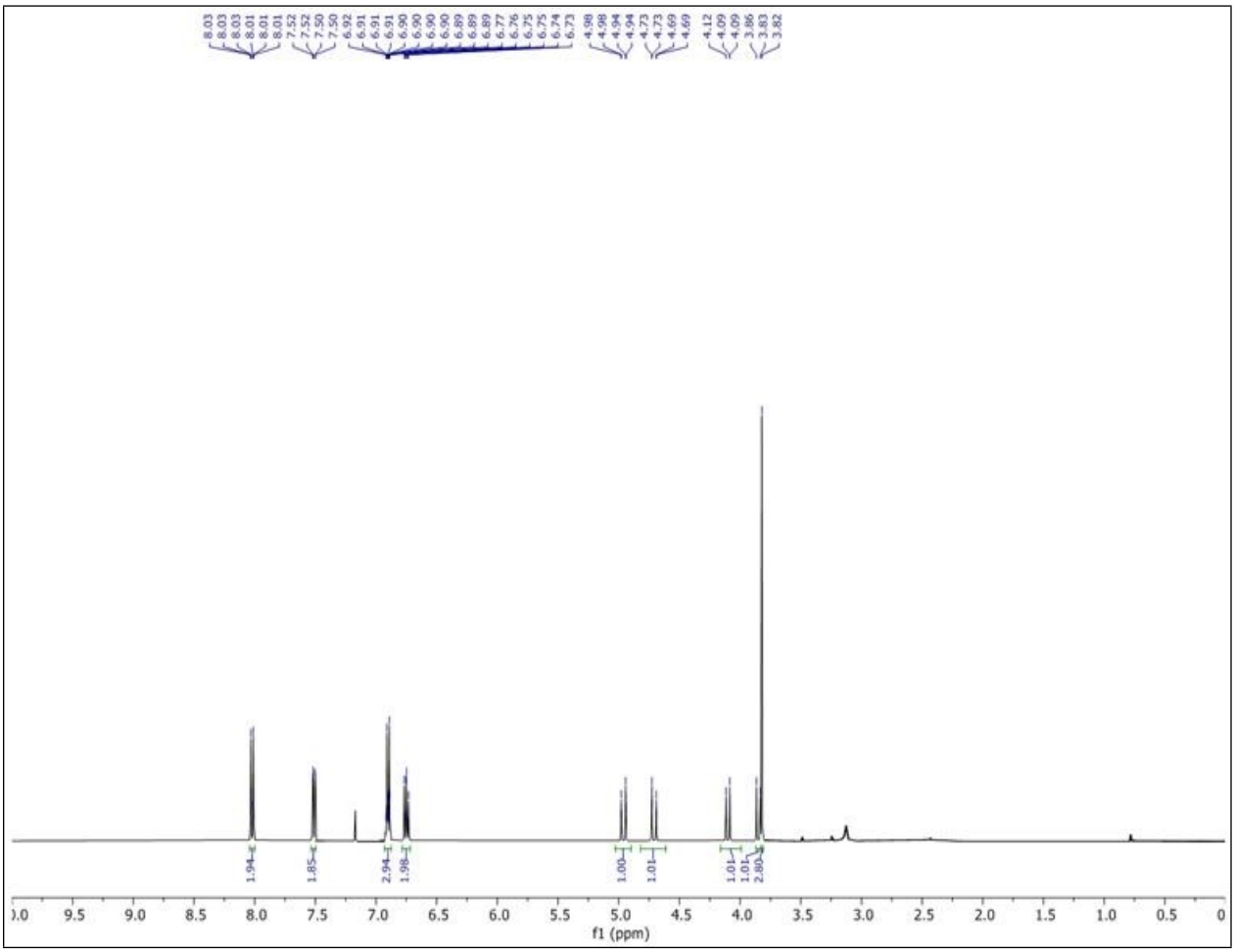

Figure S45. ^{1}H NMR spectra of **5c** in $CDCl_3$.

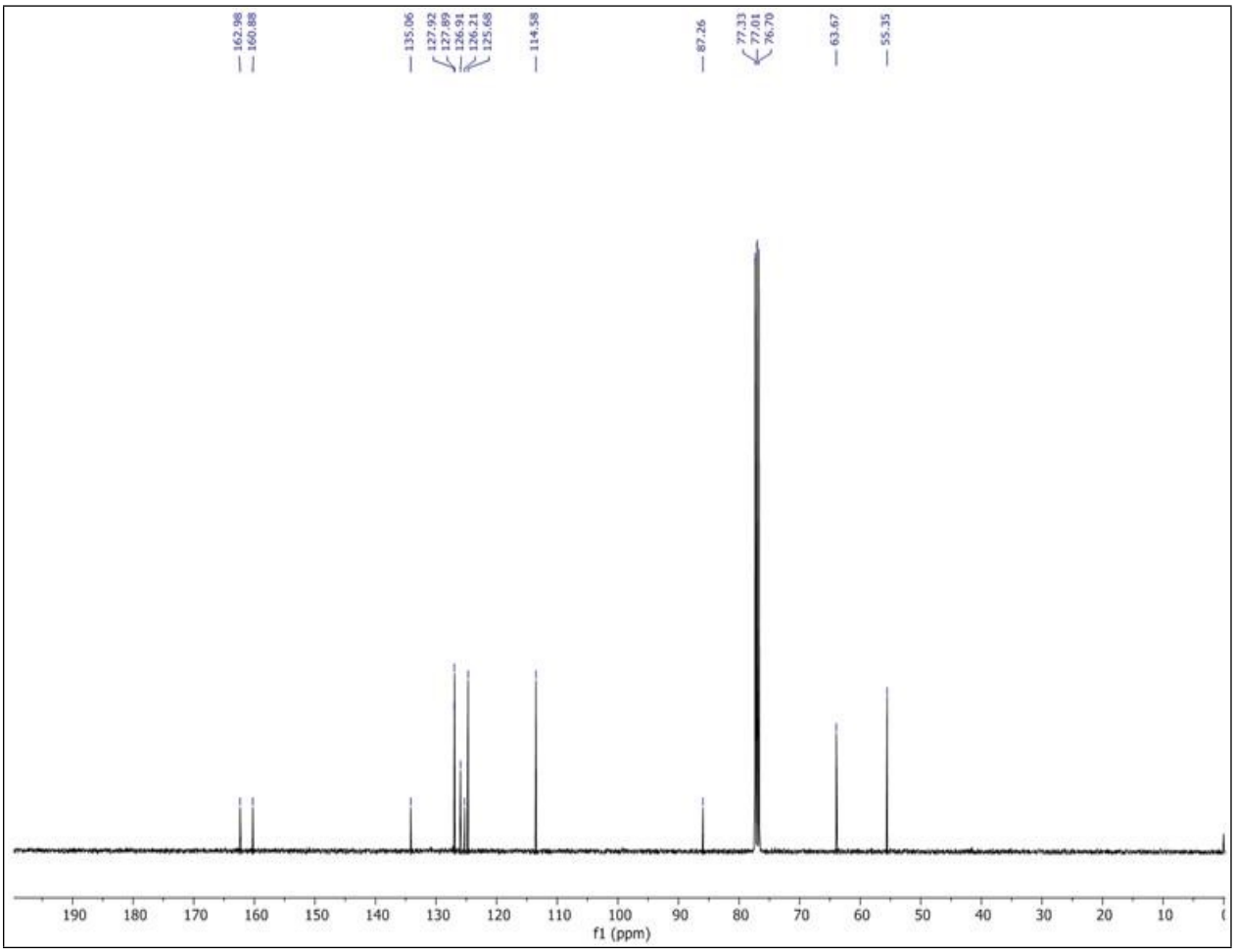

Figure S46. ^{13}C NMR spectra of **5c** in $CDCl_3$.

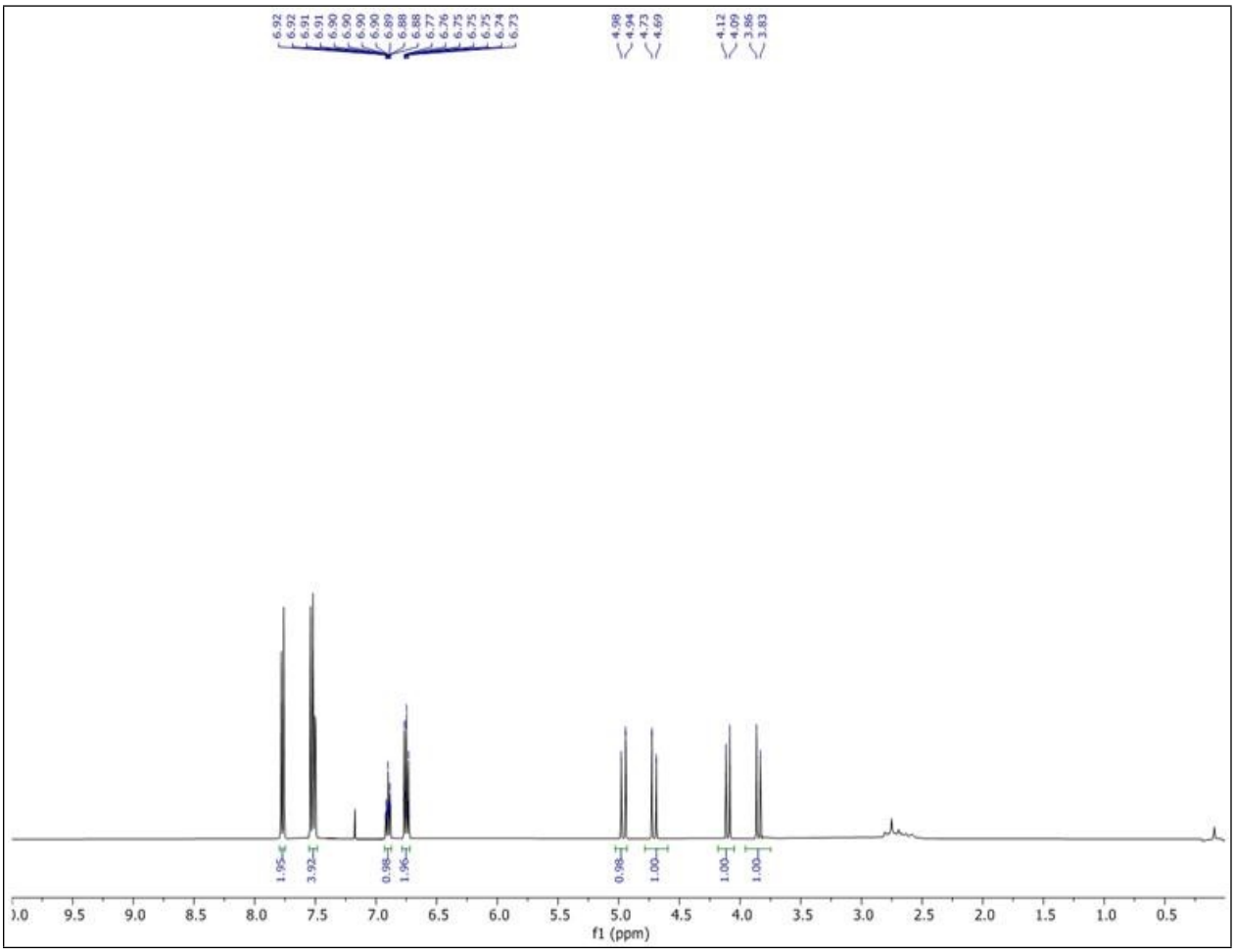

Figure S47. ^{1}H NMR spectra of **5d** in $CDCl_3$.

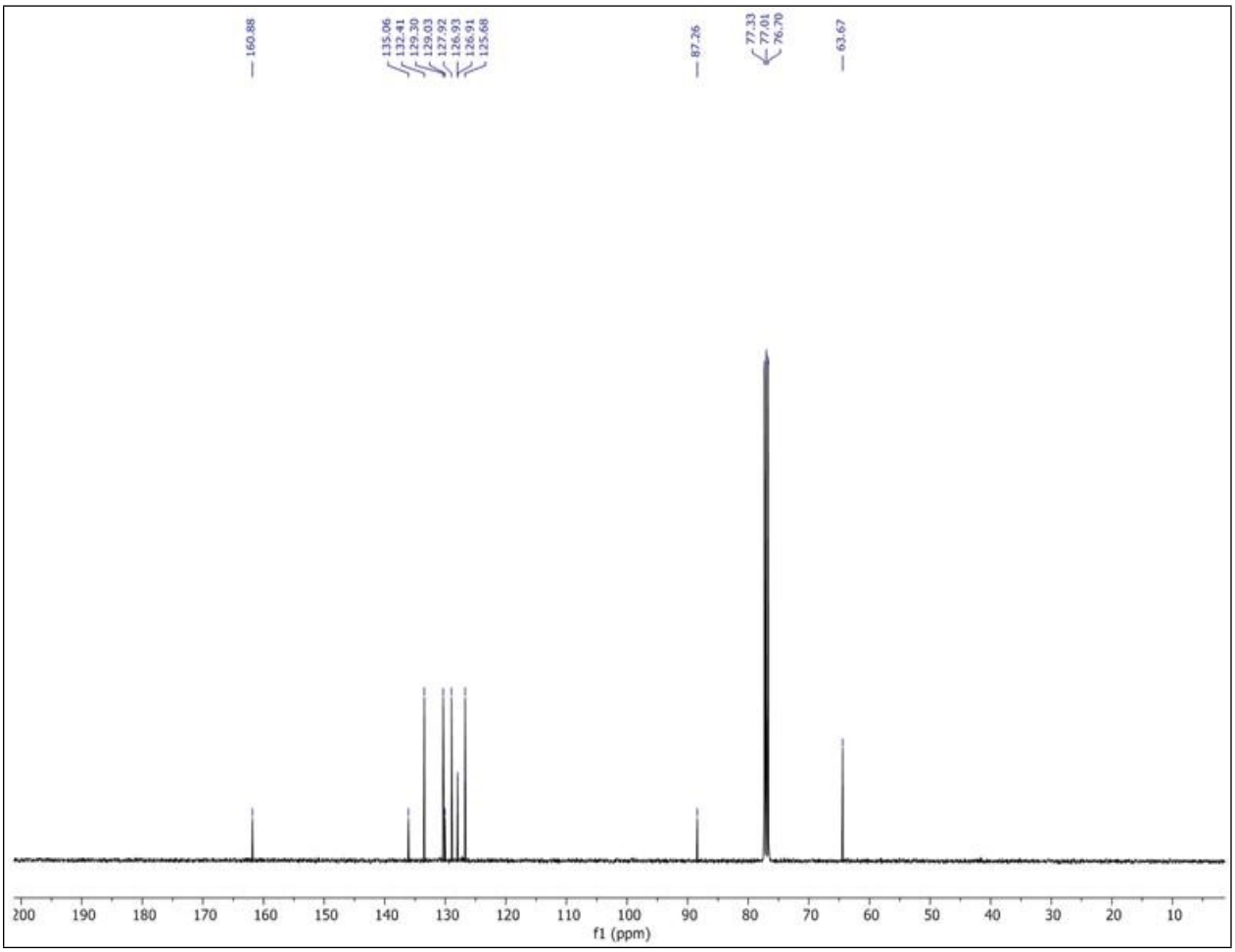

Figure S48. ^{13}C NMR spectra of **5d** in $CDCl_3$.

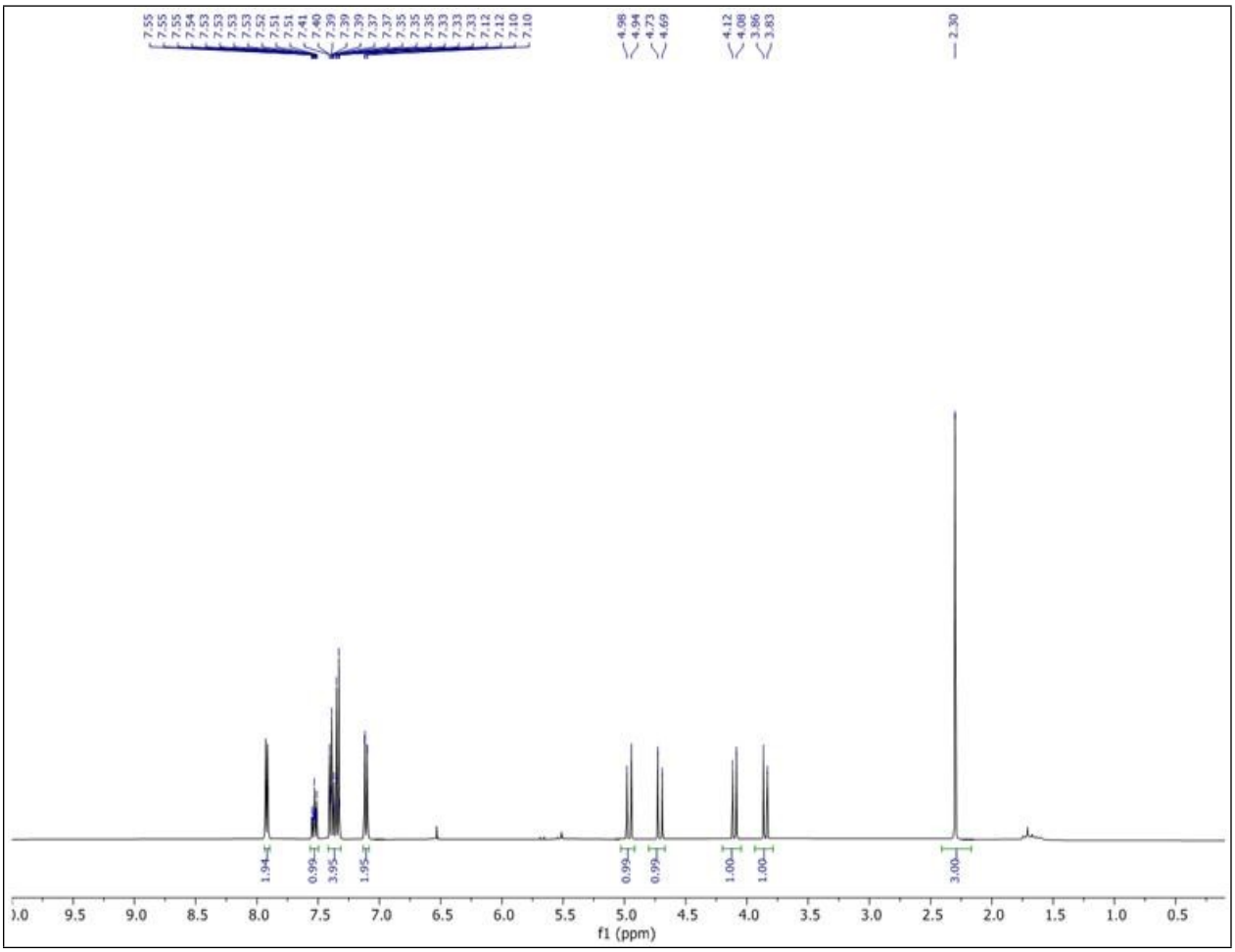

Figure S49. ^{1}H NMR spectra of **5e** in $CDCl_3$.

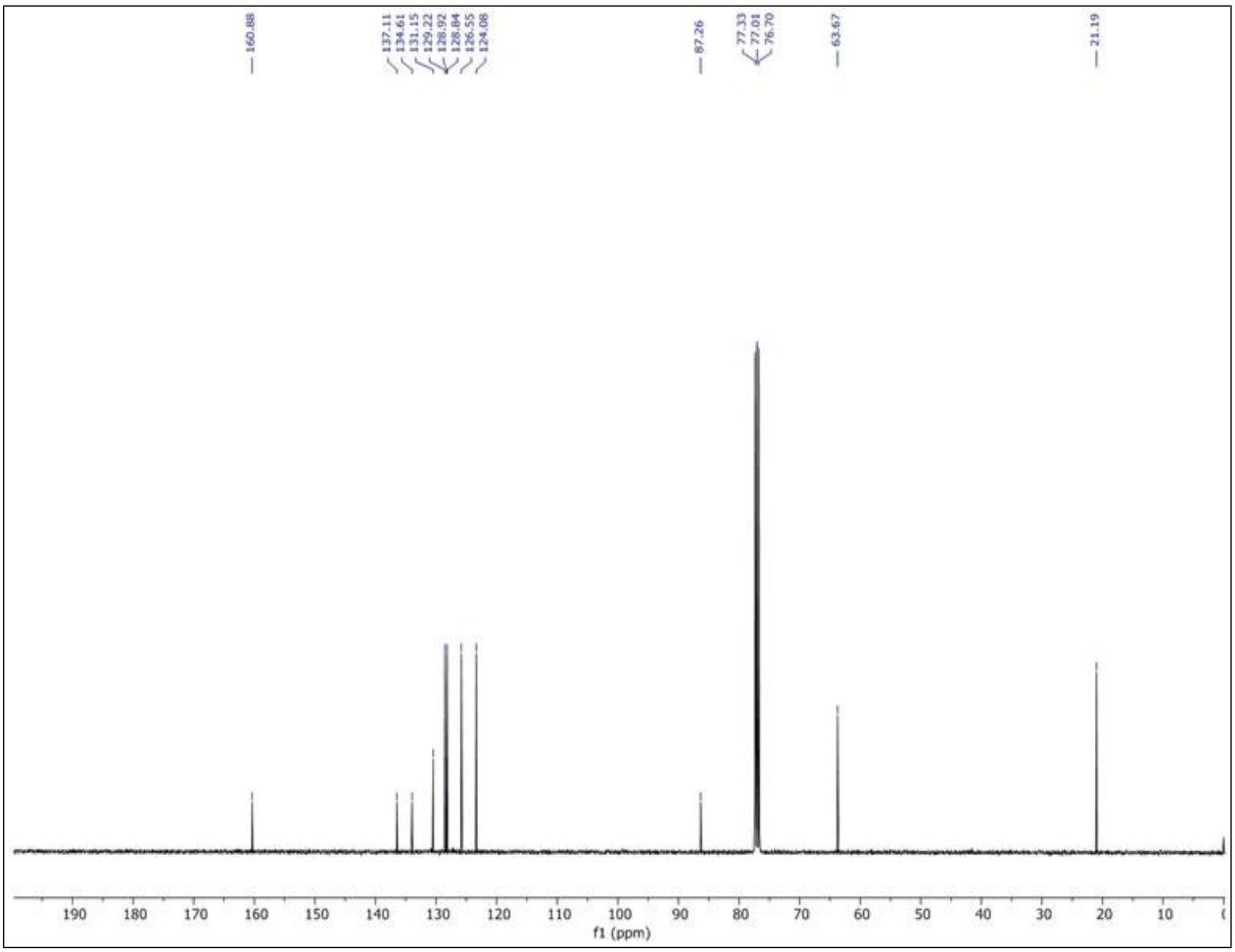

Figure S50. ^{13}C NMR spectra of **5e** in $CDCl_3$.

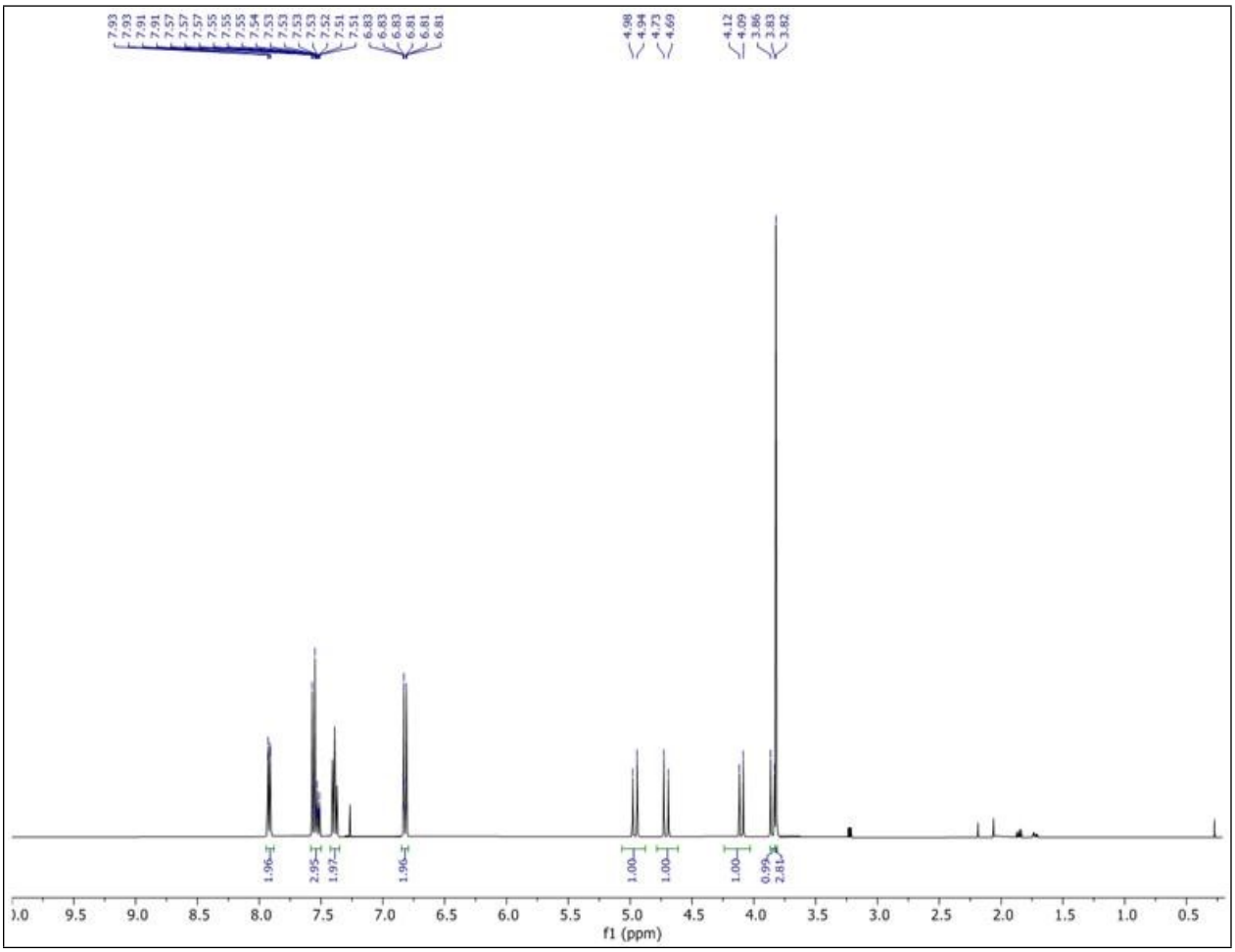

Figure S51. ^{1}H NMR spectra of **5f** in $CDCl_3$.

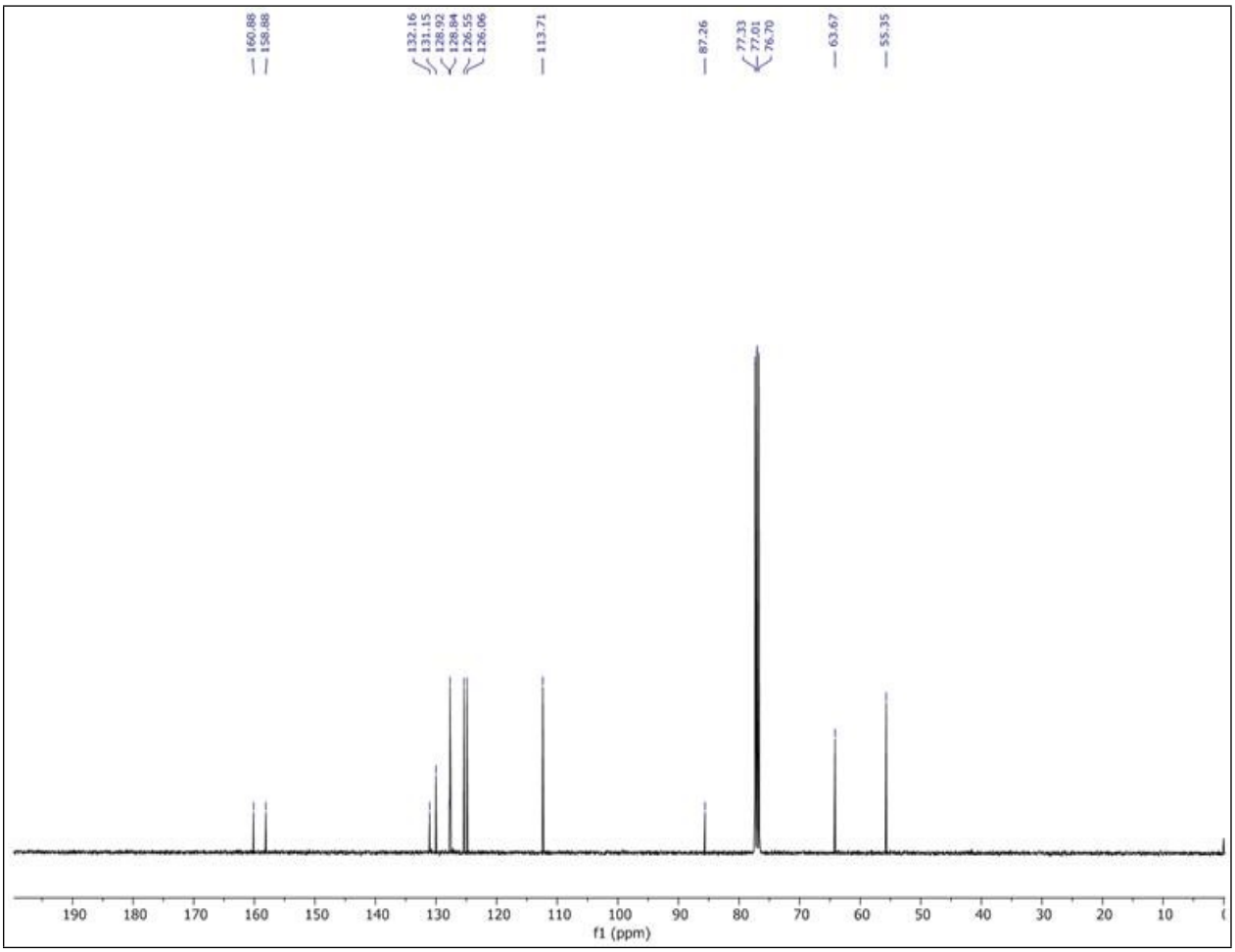

Figure S52. ^{13}C NMR spectra of **5f** in $CDCl_3$.

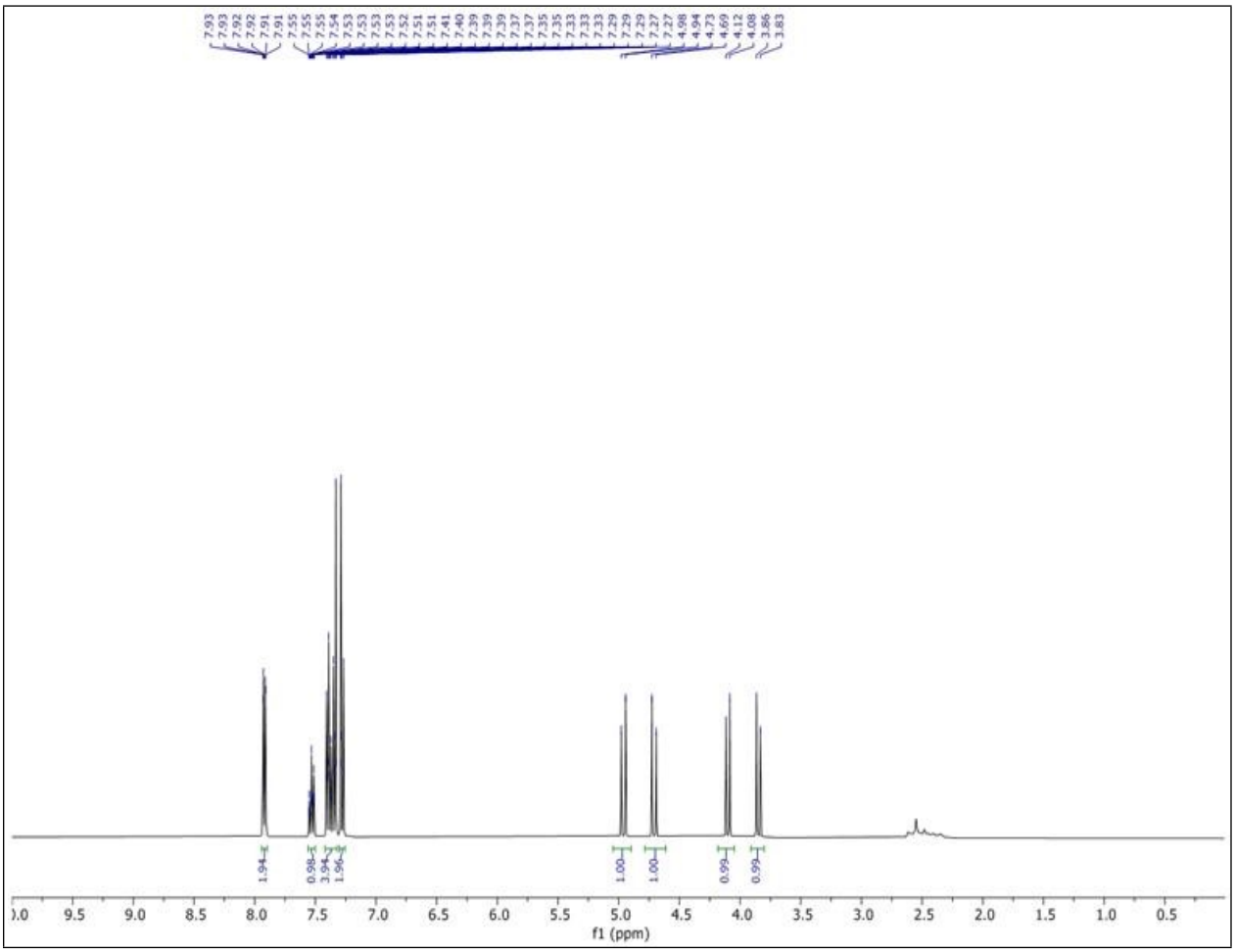

Figure S53. ^{1}H NMR spectra of **5g** in $CDCl_3$.

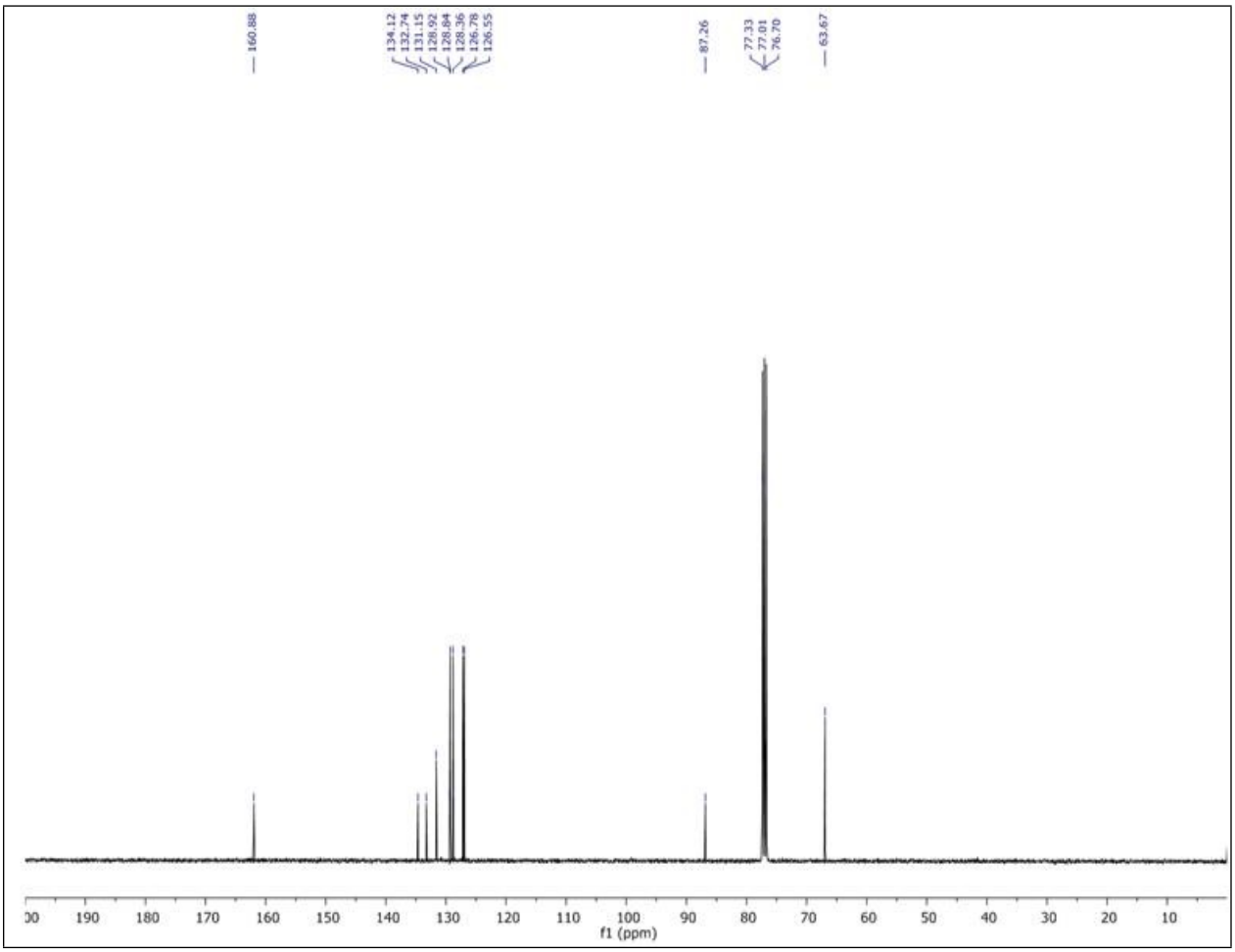

Figure S54. ^{13}C NMR spectra of **5g** in $CDCl_3$.

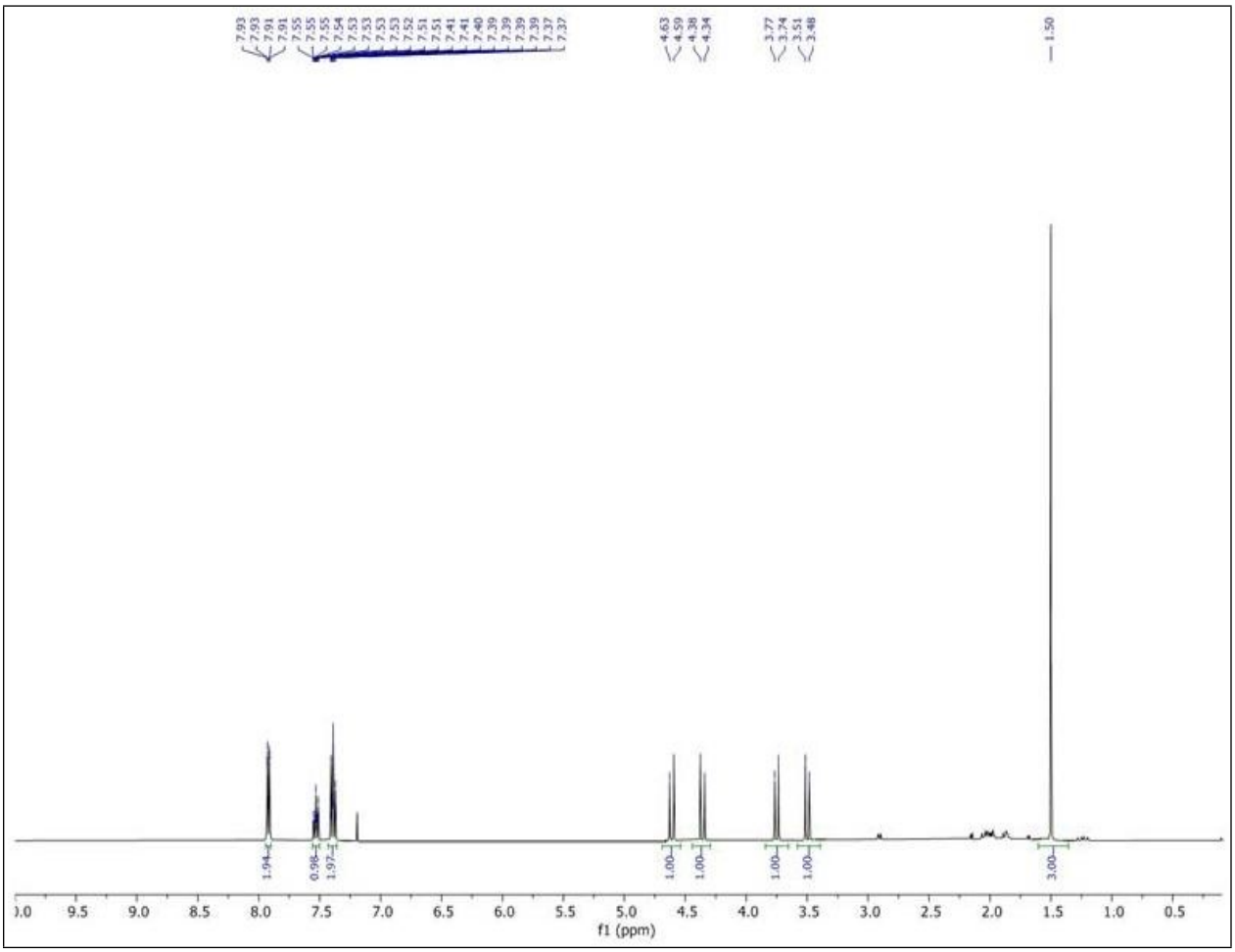

Figure S55. ^{1}H NMR spectra of **5h** in $CDCl_3$.

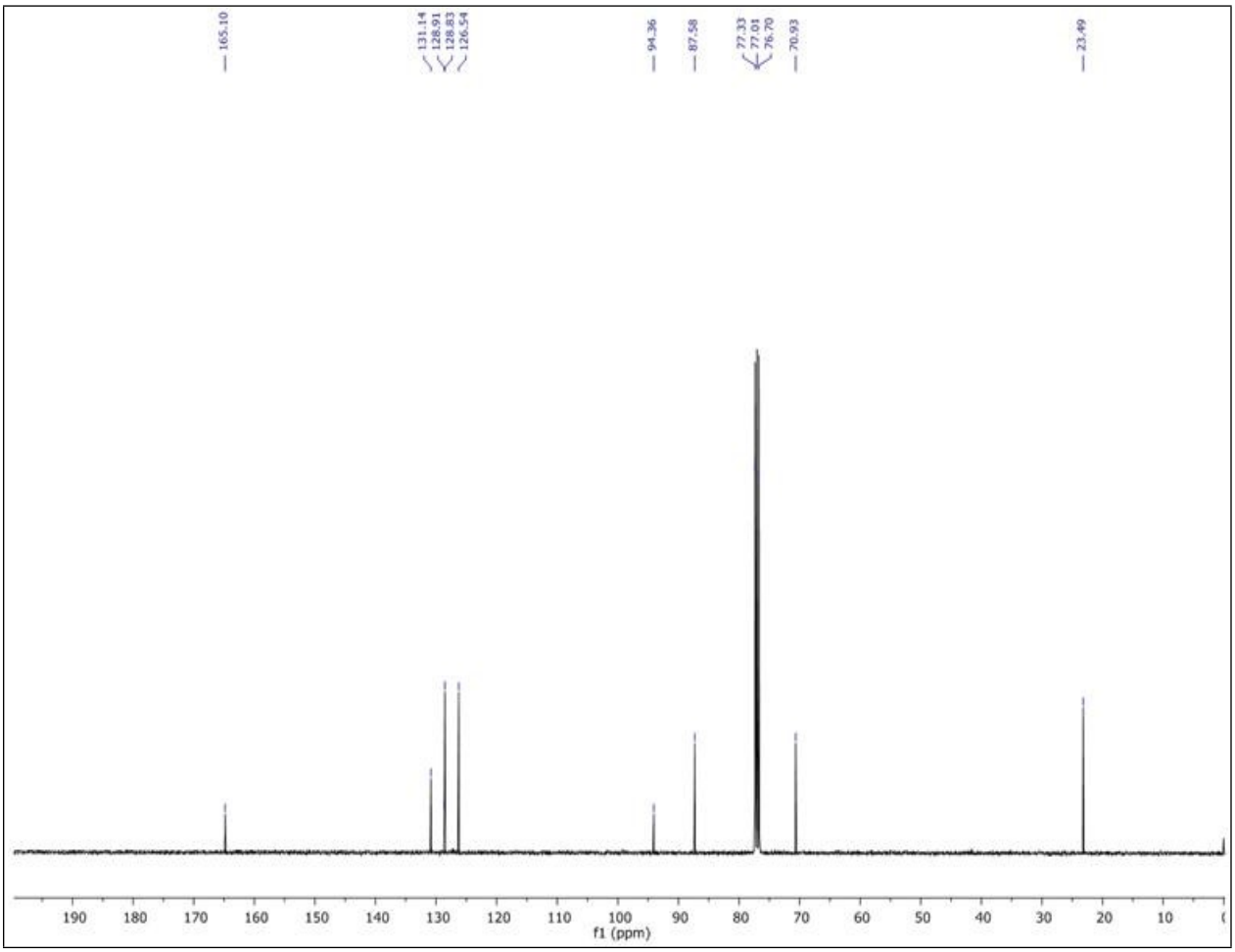

Figure S56. ^{13}C NMR spectra of **5h** in $CDCl_3$.

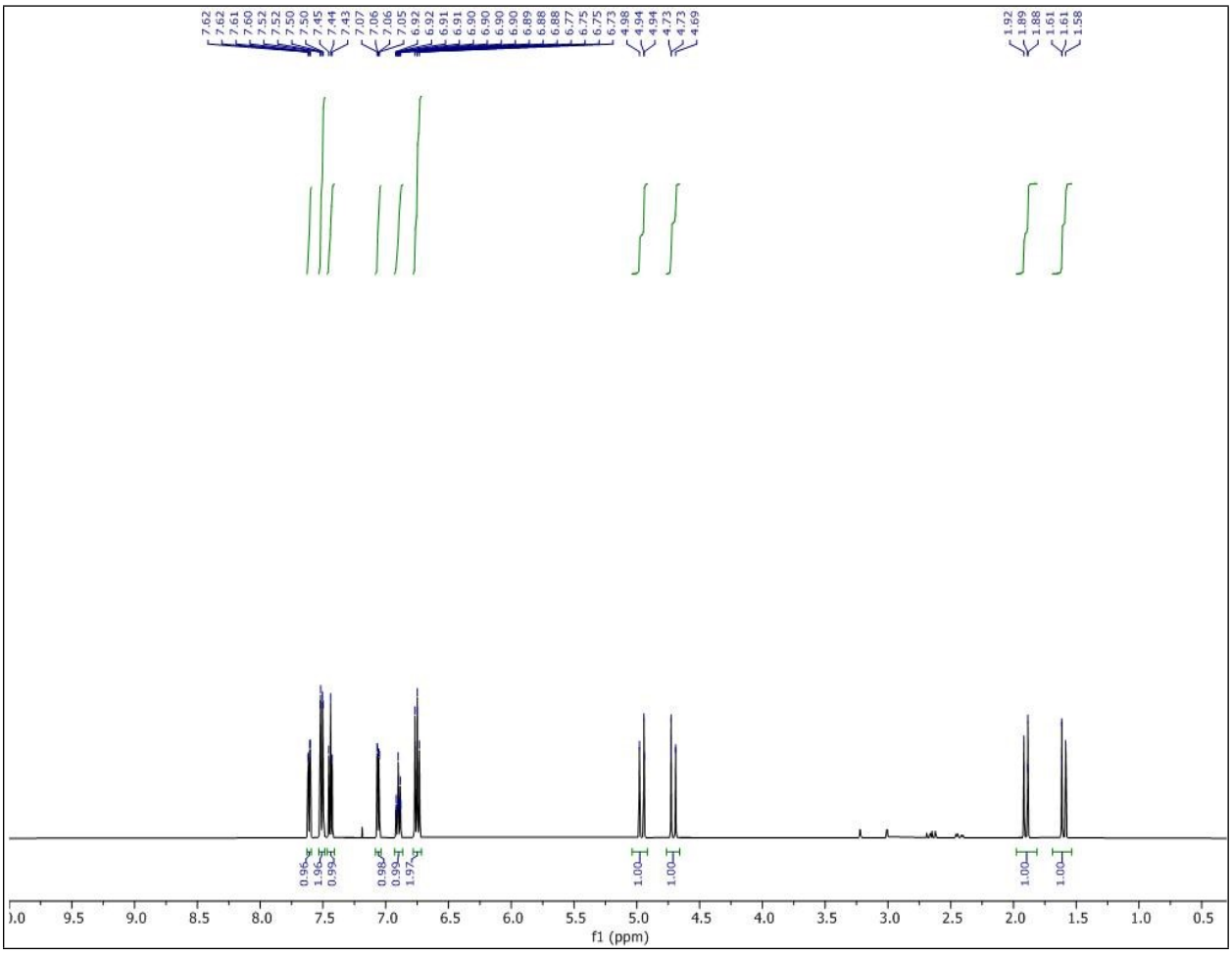

Figure S57. ^{13}C NMR spectra of **5i** in $CDCl_3$.

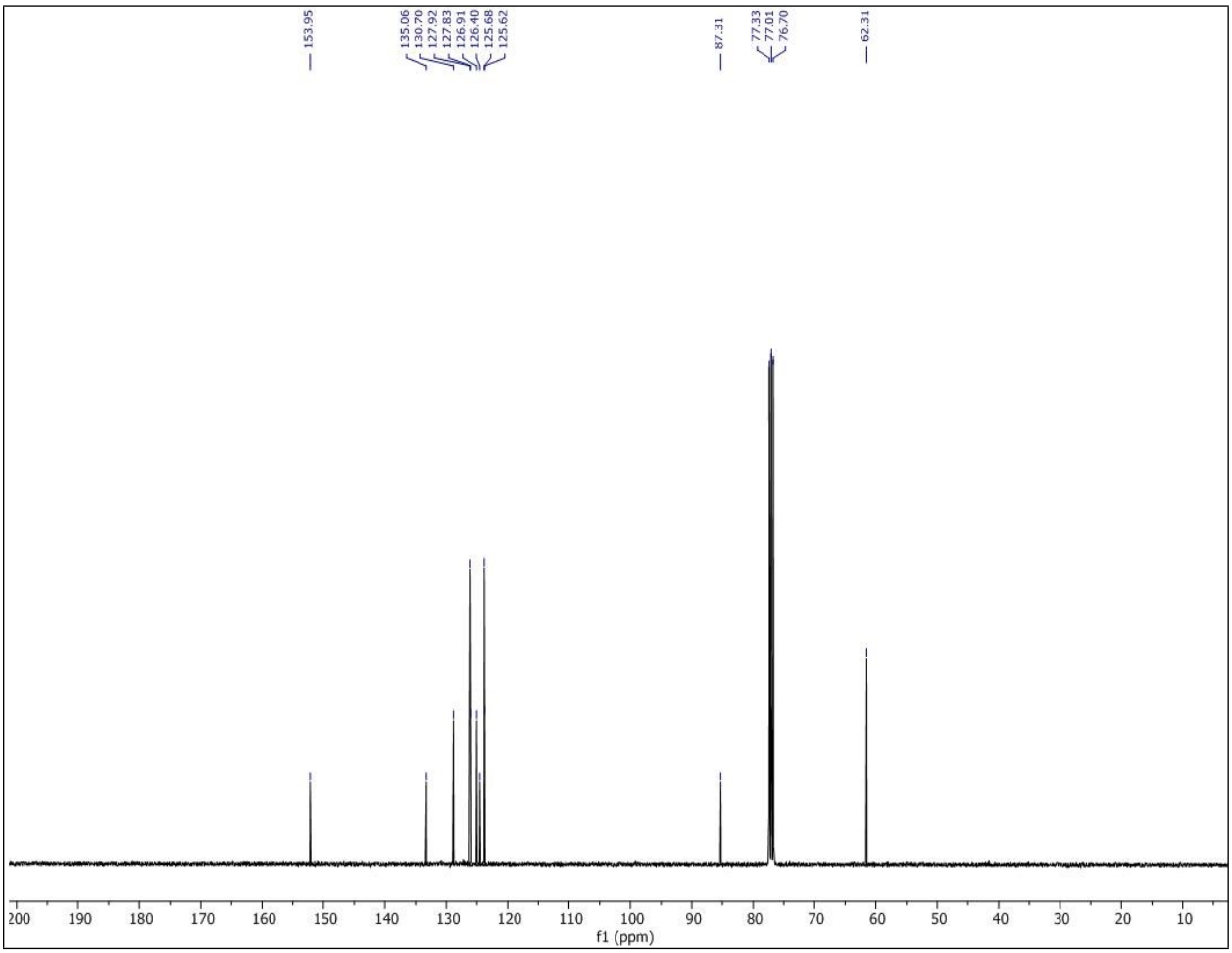

Figure S58. ^{13}C NMR spectra of **5i** in $CDCl_3$.

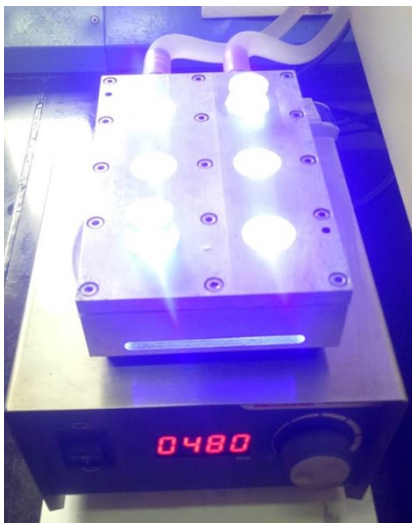

Figure S59. Pictorial diagram of reaction setup.