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A practical carbamoylsilane-based synthesis of β-arylidene *N*-methoxymethyl α-siloxy carboxamides from α,β-enones

Minggang Zhao, Fei Ma and Jianxin Chen

I Experimental section

^{1}H (600 MHz) and ^{13}C-{^{1}H} (150.8 MHz) NMR spectra were recorded on Bruker (AV600) NMR spectrometer. All spectra were recorded at room temperature in deuterated chloroform ($CDCl_3$, δ = 7.28 ppm for proton NMR, δ = 77.05 ppm for carbon NMR) unless otherwise stated using tetramethylsilane (TMS) as an internal standard. Chemical shifts are expressed in parts per million (ppm) and coupling constants in Hertz (Hz). Melting points were measured with a STUART SMP 10 melting point apparatus and uncorrected. The monitoring of reaction and checking of purity of the product were done using pre-coated silica gel plates (Merck 60 PF_{254}). Column chromatography was performed using Merck silica gel 200-300 mesh and ethyl acetate–petroleum ether elution. Visualization was achieved by UV (254 nm) light detection and iodine staining.

2. General procedure for aminocarbonylation reaction

A Schlenk tube fitted with a Teflon vacuum stopcock and micro stirring bar was flame-heated under vacuum and refilled with Ar. *α*,*β*-Unsaturated ketone **1** (0.5 mmol) and anhydrous toluene (1.5 ml) were added at ice bath temperature. After 15 min, *N*-methoxymethyl-*N*-methylcarbamoyl silane **2** (0.6 mmol) was added. The sealed reaction mixture was stirred at 105 °C until no carbamoylsilane **2** could be detected by TLC. Volatiles were removed *in vacuo* to give the crude product, which was purified by column chromatography on silica gel using petroleum ether–ethyl acetate as eluent to yield products **3**.

II ^{1}H NMR data, ^{13}C NMR data, IR and elemental analysis data of 3a-i

***N*-Methoxymethyl-*N*-methyl-2,4-diphenyl-2-(trimethylsiloxy)but-3-enamide (3a).** Yellow thick liquid. IR: 1658, 1246, 1051 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53–7.20 (m, 11 H), 5.93 (t, J = 18 Hz, 1 H), 4.99–4.56 (m, 2 H), 3.34, 2.95 (ss, 3 H), 2.82, 2.57 (ss, 3 H), 0.25, 0.23 (ss, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 174.1, 173.8, 142.1, 141.6, 136.6, 133.9, 133.6, 132.8, 132.6, 128.5, 128.2, 127.8, 127.6, 127.5, 126.7, 125.8, 125.7, 82.3, 82.2, 79.6, 56.2, 54.2, 34.0, 32.0, 2.0. Anal. Calcd for $C_{22}H_{29}NO_3Si$: C, 68.89; H, 7.62; N, 3.65. found: C, 68.72; H, 7.41; N, 3.42.

***N*-Methoxymethyl-*N*-methyl-4-(4-methylphenyl)-2-phenyl-2-(trimethylsiloxy)but-3-enamide (3b).** Yellow thick liquid. IR: 1658, 1232, 1042 cm^{-1}. ^{1}H NMR: δ 7.39–7.09 (m, 10H), 5.90 (t, J = 18 Hz, 1 H), 4.99–4.57 (m, 2 H), 3.34, 2.96 (ss, 3 H), 2.83, 2.57 (ss, 3 H), 2.32 (s, 3 H), 0.25, 0.23 (ss, 9 H). ^{13}C NMR: δ 174.1, 173.8, 142.1, 141.6, 136.6, 133.9, 133.6, 132.8, 132.6, 128.5, 128.2, 127.6, 127.5, 126.7, 125.8, 125.7, 82.3, 82.2, 79.6, 56.2, 54.2, 34.0, 32.0, 21.2, 2.0. Anal. Calcd for $C_{23}H_{31}NO_3Si$: C, 69.48; H, 7.86; N, 3.52. Found: C, 69.56; H, 7.65; N, 3.34.

***N*-Methoxymethyl-4-(4-methoxyphenyl)-*N*-methyl-2-phenyl-2-(trimethylsiloxy)but-3-enamide (3c).** Yellow thick liquid. IR: 1643, 1231, 1065 cm^{-1}. ^{1}H NMR: δ 7.50–6.81 (m, 10 H), 5.83 (t, J = 16.8 Hz, 1 H), 4.97–4.55 (m, 2 H), 3.78 (s, 3 H), 3.32, 2.93 (ss, 3 H), 2.81, 2.55 (ss, 3 H), 0.22, 0.20 (ss, 9 H). ^{13}C NMR: δ 174.2, 173.9, 159.4, 142.2, 141.7, 132.4, 132.2, 131.7, 131.4, 129.4, 128.1, 127.9, 127.5, 127.4, 125.9, 125.7, 113.9, 82.4, 82.3, 79.6, 56.2, 55.2, 54.1, 33.9, 32.0, 2.0. Anal. Calcd for $C_{23}H_{31}NO_4Si$: C, 69.48; H, 7.86; N, 3.52. Found: C, 69.21; H, 7.89; N, 3.65.

4-(4-Chlorophenyl)-*N*-methoxymethyl-*N*-methyl-2-phenyl-2-(trimethylsiloxy)but-3-enamide (3d). Yellow thick liquid. IR: 1658, 1260, 1062 cm^{-1}. ^{1}H NMR: δ 7.50–7.14 (m, 10 H), 5.83 (t, J = 16.8 Hz, 1 H), 4.98–4.53 (m, 2 H), 3.32, 2.93 (ss, 3 H), 2.79, 2.55 (ss, 3 H), 0.22, 0.20 (ss, 9 H). ^{13}C NMR: δ 174.0, 173.6, 141.8, 141.3, 135.1, 134.6, 134.4, 133.4, 131.5, 131.3, 128.7, 128.3, 127.9, 127.7, 127.6, 125.7, 125.6, 82.2, 82.1, 79.6, 77.3, 77.1, 76.9, 56.2, 54.2, 33.9, 32.0, 2.0, 1.9. Anal. Calcd for $C_{22}H_{28}NO_3SiCl$: C, 63.21; H, 7.50; N, 3.35. Found: C, 63.32; H, 7.36; N, 3.16.

***N*-Methoxymethyl-*N*-methyl-4-(4-nitrophenyl)-2-phenyl-2-(trimethylsiloxy)but-3-enamide (3e).** Yellow thick liquid. IR: 1644, 1246, 1108 cm^{-1}. ^{1}H NMR: δ 8.13–7.28 (m, 10 H), 5.95 (t, J = 17.4 Hz, 1 H), 4.97–4.51 (m, 2 H), 3.31, 2.93 (ss, 3 H), 2.78, 2.55 (ss, 3 H), 0.22, 0.21 (ss, 9 H). ^{13}C NMR: δ 173.6, 173.3, 147.1, 143.1, 141.3, 140.8, 138.8, 138.7, 130.3, 130.0, 128.4, 128.0, 127.8, 127.6, 127.5, 127.2, 125.6, 125.4, 123.9, 122.2, 82.0, 81.9, 79.6, 56.3, 54.3, 33.9, 32.1, 2.0, 1.9. Anal. Calcd for $C_{22}H_{28}N_2O_5Si$: C, 61.66; H, 6.59; N, 6.54. Found: C, 61.64; H, 6.35; N, 6.69.

***N*-Methoxymethyl-*N*-methyl-2,6-diphenyl-2-(trimethylsiloxy)hexa-3,5-dienamide (3f).** Yellow thick liquid. IR: 1755，1630, 1246, 1056 cm^{-1}. ^{1}H NMR: δ 7.36–7.19 (m, 10 H), 6.86–6.72 (m, 2 H), 6.39–6.34 (m, 1 H), 5.70 (s, 1 H), 4.95–4.53 (m, 2 H), 3.31, 2.92 (dd, 3 H), 2.78, 2.53 (dd, 3 H), 0.22 (s, 9 H). ^{13}C NMR: δ 174.0, 173.7, 141.9, 141.4, 137.7, 137.5, 137.1, 133.5, 133.3, 133.1, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 127.6, 127.5, 126.4, 125.7, 125.6, 82.3, 82.1, 79.6, 56.2, 54.1, 33.9, 32.0, 2.0. Anal. Calcd for $C_{24}H_{31}NO_3Si$: C, 70.38; H, 7.63; N, 3.42. Found: C, 70.23; H, 7.45; N, 3.25.

***N*-Methoxymethyl-*N*-methyl-4-phenyl-2-(2-phenylvinyl)-2-(trimethylsiloxy)but-3-enamide (3g).** Yellow thick liquid. IR: 1768，1658, 1260, 890 cm^{-1}. ^{1}H NMR: δ 7.49–7.28 (m, 8 H), 6.76–6.73 (m, 5 H), 5.01, 4.90 (ss, 1 H), 3.39, 3.23 (ss, 3 H), 3.15, 3.02 (ss, 3 H), 0.23 (s, 9 H). ^{13}C NMR: δ 173.5, 136.4, 131.2, 131.0, 130.6, 128.7, 128.0, 126.8, 81.3, 80.0, 56.2, 55.2, 34.5, 33.0, 30.6, 2.1. Anal. Calcd for $C_{24}H_{31}NO_3Si$: C, 70.38; H, 7.63; N, 3.42. Found: C, 70.26; H, 7.48; N, 3.32.

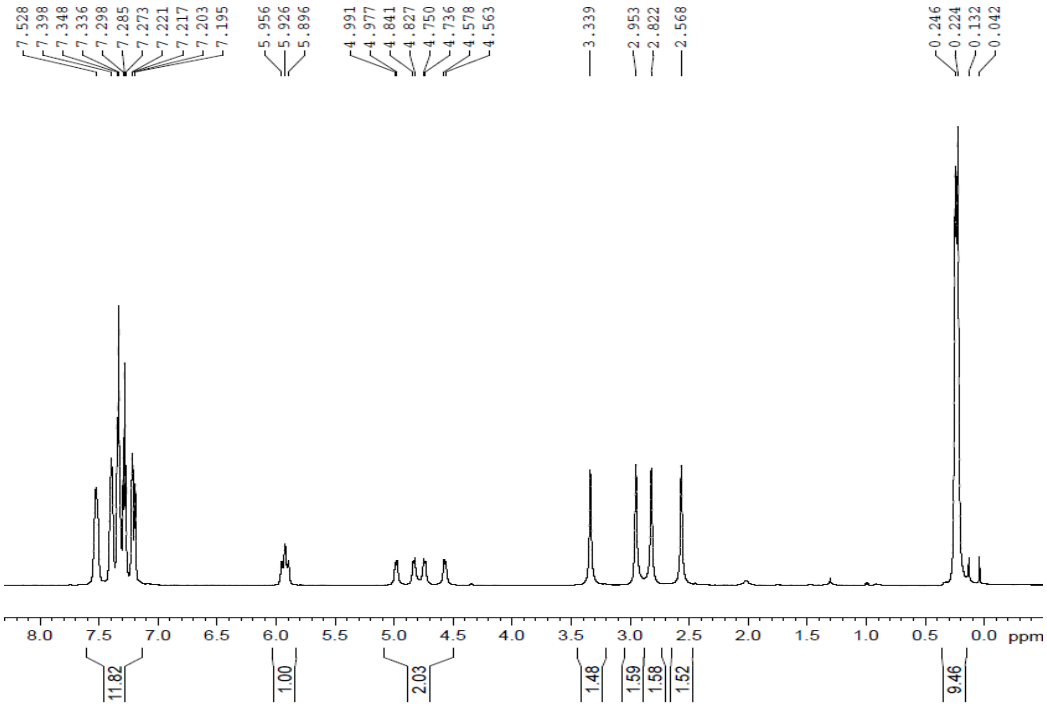
4-(2-Furyl)-*N*-methoxymethyl-*N*-methyl-2-phenyl-2-(trimethylsiloxy)but-3-enamide (3h). Brown red solid, Mp: 88.0–90.0 °C. IR: 1644, 1246, 1066 cm^{-1}. ^{1}H NMR: δ 7.47–7.28 (m, 6 H), 7.07, 7.04 (ss, 1 H), 6.29, 6.12 (ss, 2 H), 5.67 (t, J = 15.6 Hz, 1 H), 4.94–4.54 (m, 2 H), 3.30, 2.91 (ss, 3 H), 2.77, 2.54 (ss, 3 H), 0.21 (s, 9 H). ^{13}C NMR: δ 173.8, 173.5, 152.4, 142.3, 141.5, 141.1, 132.5, 132.2, 128.2, 127.7, 127.6, 125.8, 125.7, 121.0, 120.9, 111.2, 108.7, 82.3, 82.2, 79.6, 56.2, 54.1, 33.9, 32.0, 1.9. Anal. Calcd for $C_{20}H_{27}NO_4Si$: C, 63.97; H, 7.25; N, 3.73. Found: C, 63.87; H, 7.43; N, 3.62.

***N*-Methoxymethyl-*N*-methyl-2-phenyl-4-(2-thienyl)-2--(trimethylsiloxy)but-3-enamide (3i).** Yellow thick liquid. IR: 1658, 1231, 1055 cm^{-1}. ^{1}H NMR: δ 7.32–6.81 (m, 9 H), 5.99 (t, J = 13.8 Hz, 1 H), 4.97–4.53 (m, 2 H), 3.31, 2.93 (ss, 3 H), 2.79, 2.55 (ss, 3 H), 0.24, 0.22 (ss, 9 H). ^{13}C NMR: δ 173.9, 173.5, 141.8, 141.6, 141.1, 133.4, 133.2, 128.3, 127.7, 127.6, 127.3, 126.3, 126.1, 126.0, 125.8, 125.7, 124.8, 82.3, 82.2, 79.6, 56.2, 54.2, 33.9, 32.0, 2.0. Anal. Calcd for $C_{20}H_{27}NO_3SSi$: C, 61.66; H, 6.99; N, 3.60. Found: C, 61.43; H, 7.12; N, 3.42.

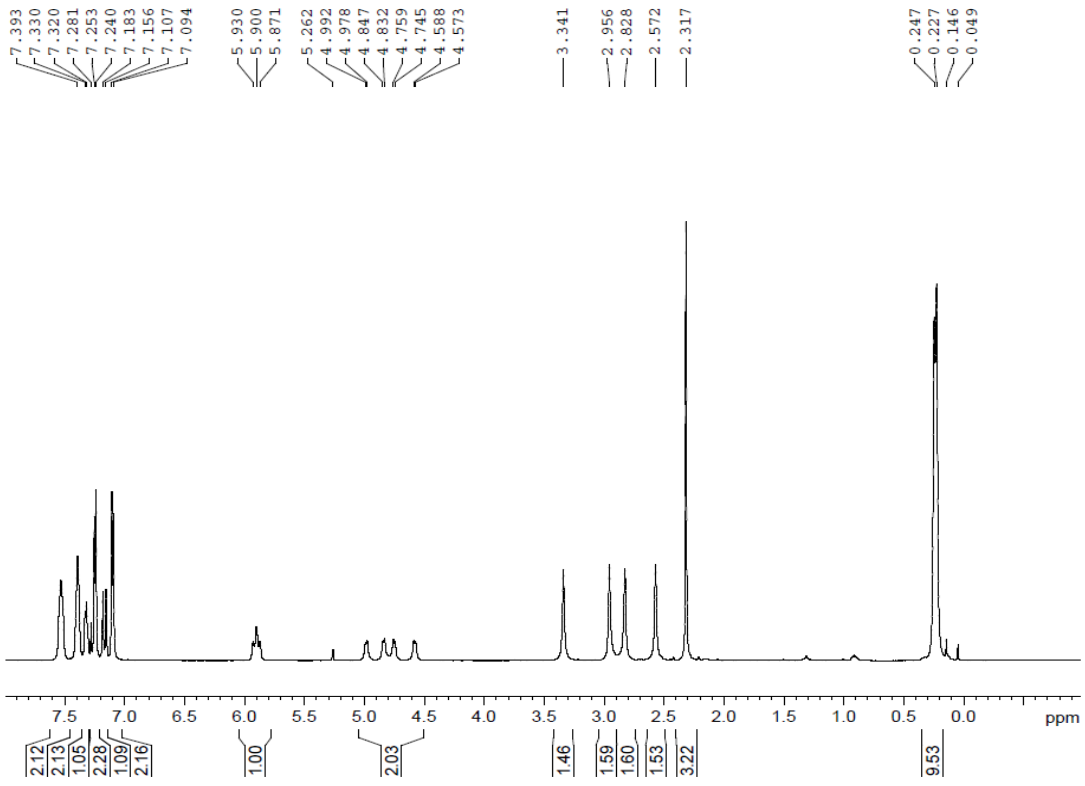
III ^{1}H NMR and ^{13}C NMR spectra of 3a-i

1. ^{1}H NMR spectra of 3a-i (^{1}H NMR (600 MHz) spectra were recorded on a Bruker AR600 MHz spectrometer in $CDCl_3$, with TMS as an internal standard).

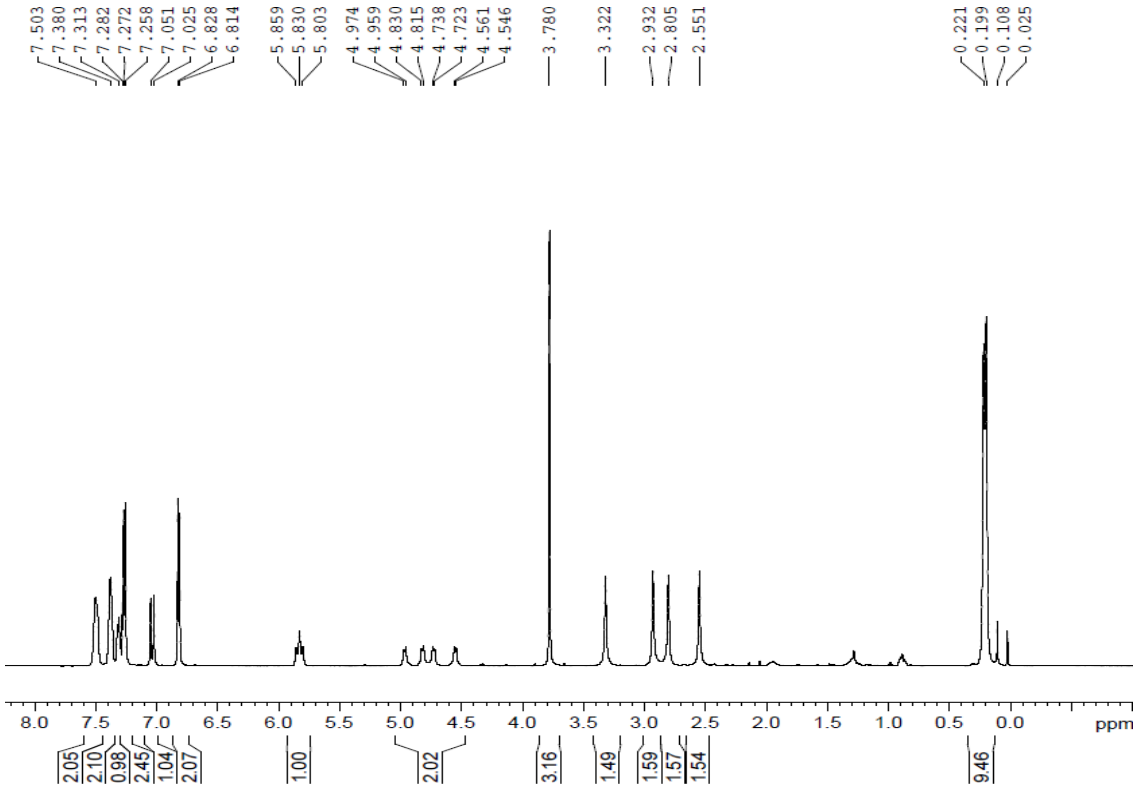
^{1}H NMR of **3a**



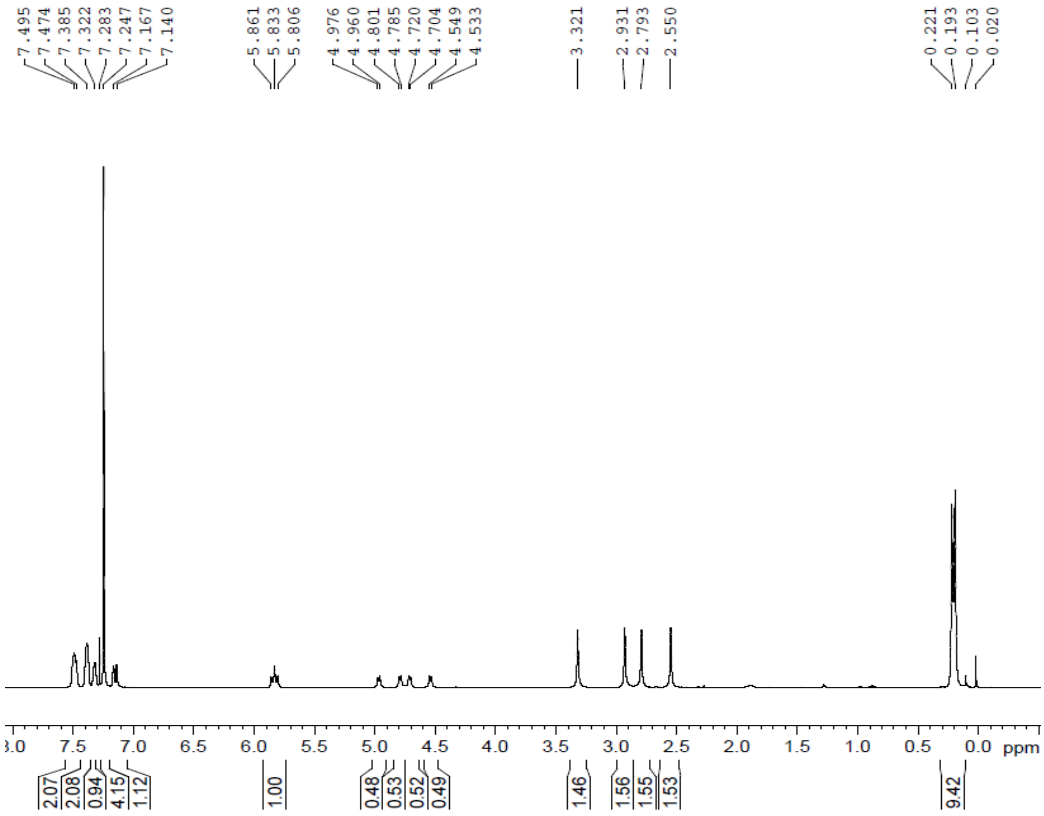
^{1}H NMR of **3b**



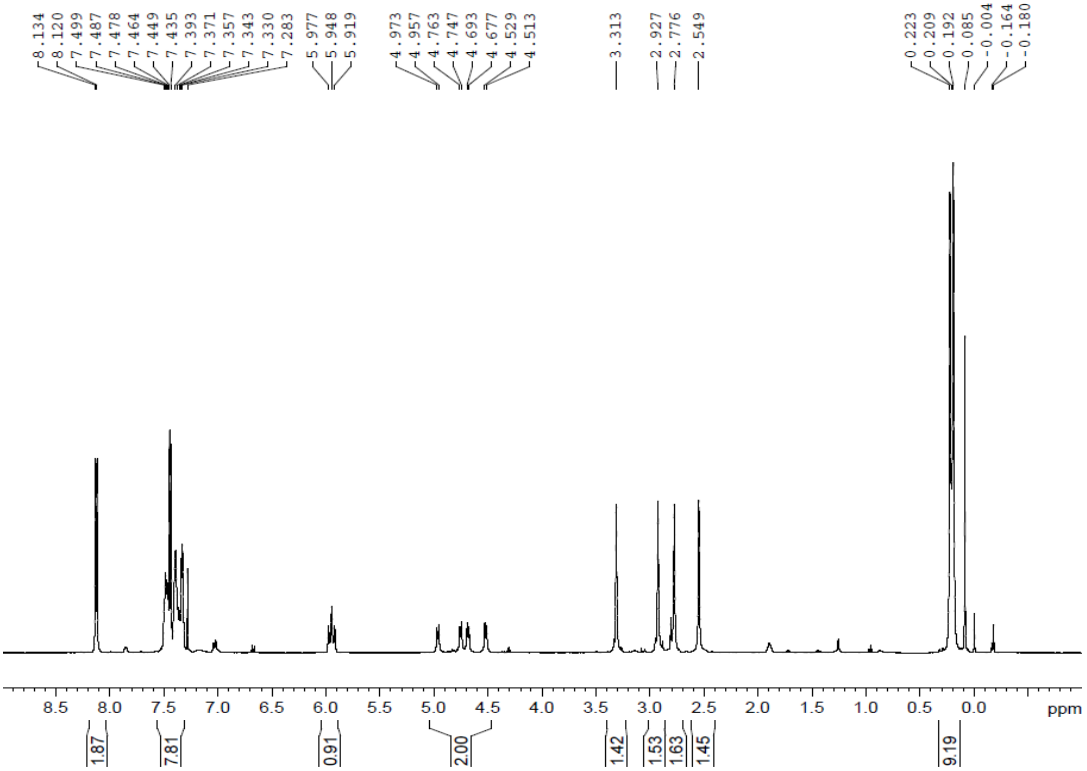
^{1}H NMR of **3c**



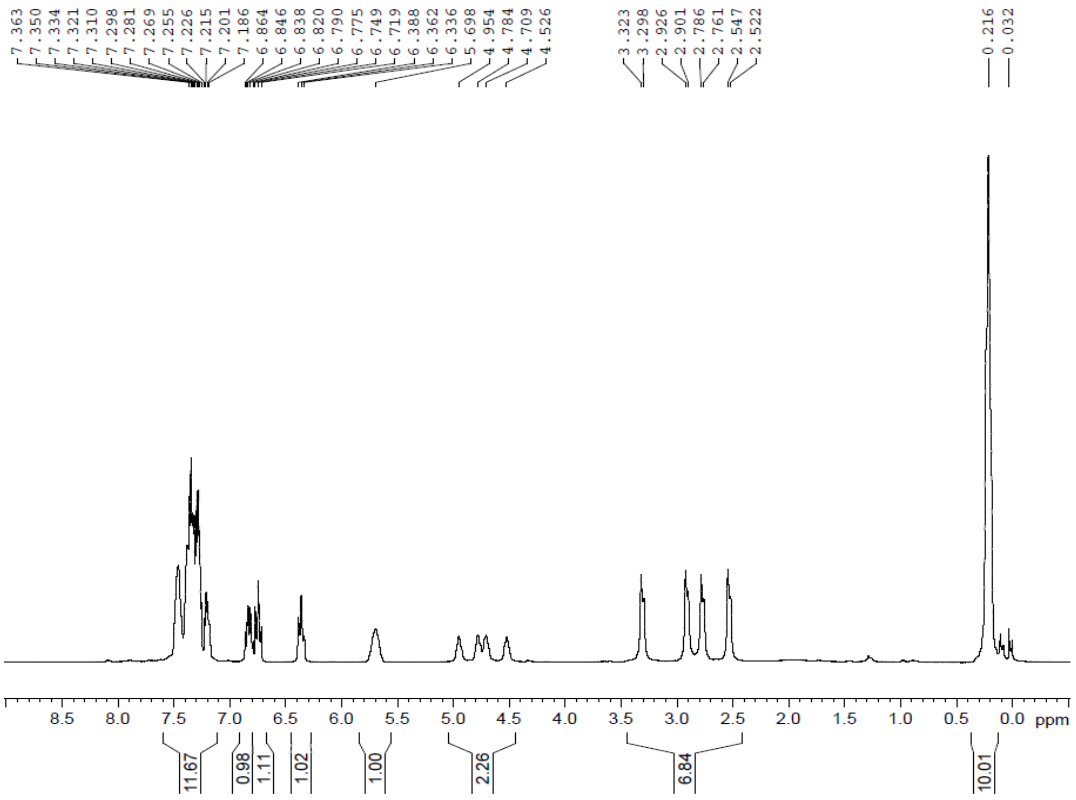
^{1}H NMR of **3d**



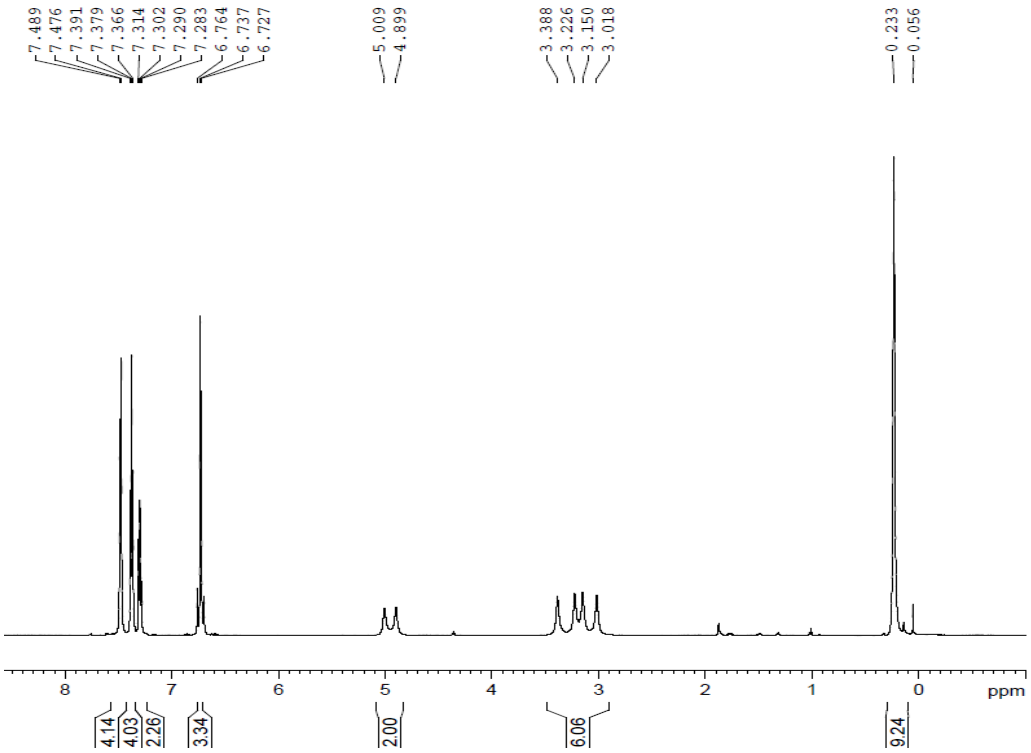
^{1}H NMR of **3e**



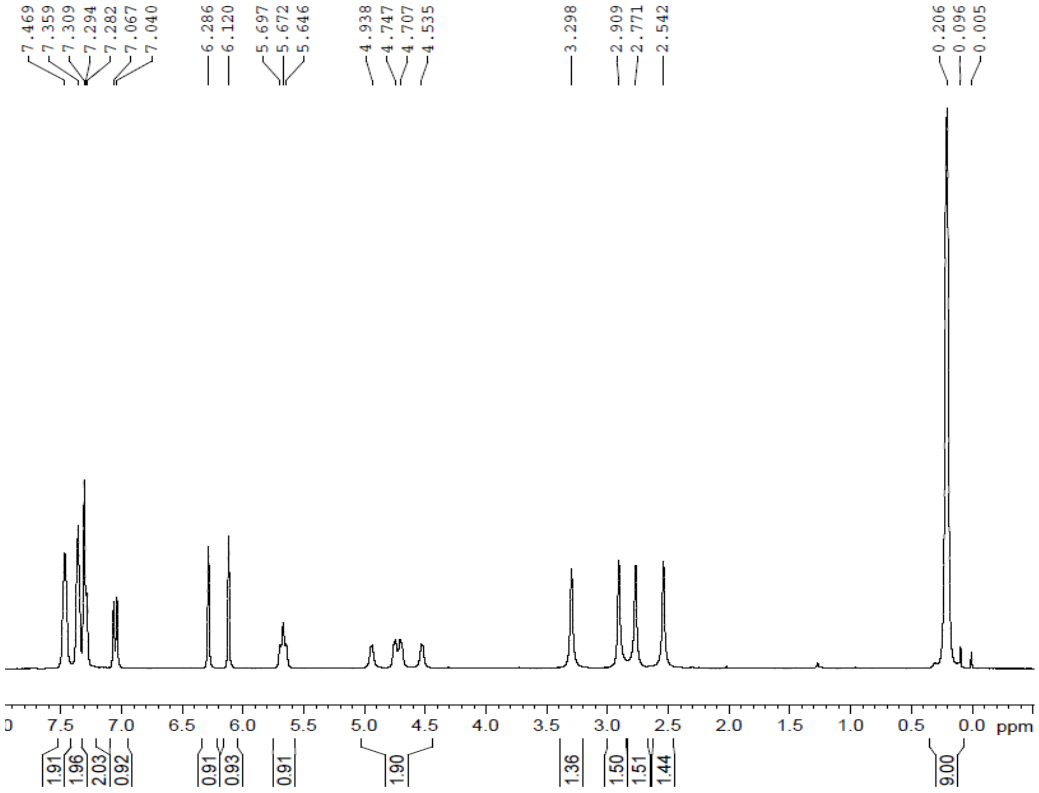
^{1}H NMR of **3f**



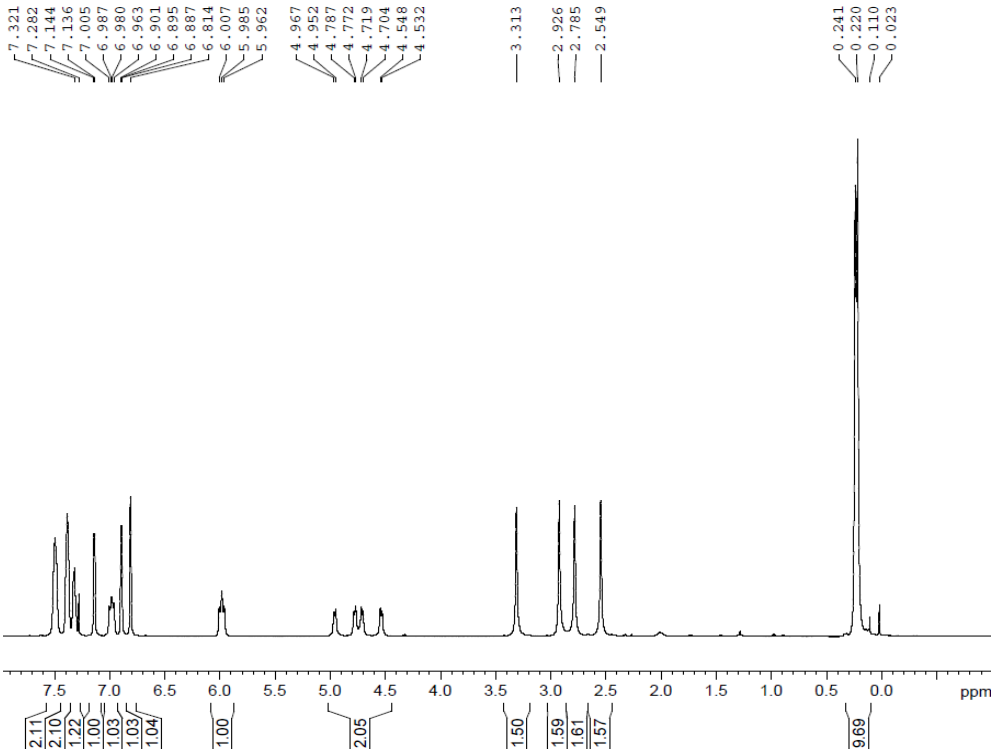
^{1}H NMR of **3g**



^{1}H NMR of **3h**

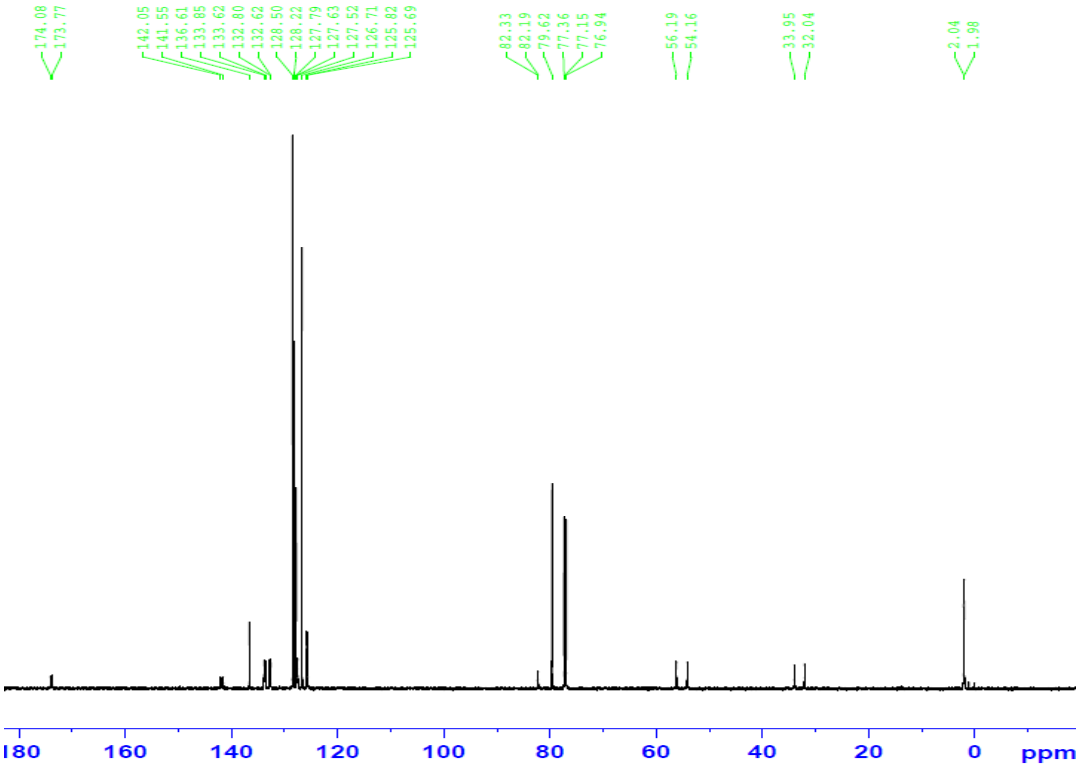


^{1}H NMR of **3i**

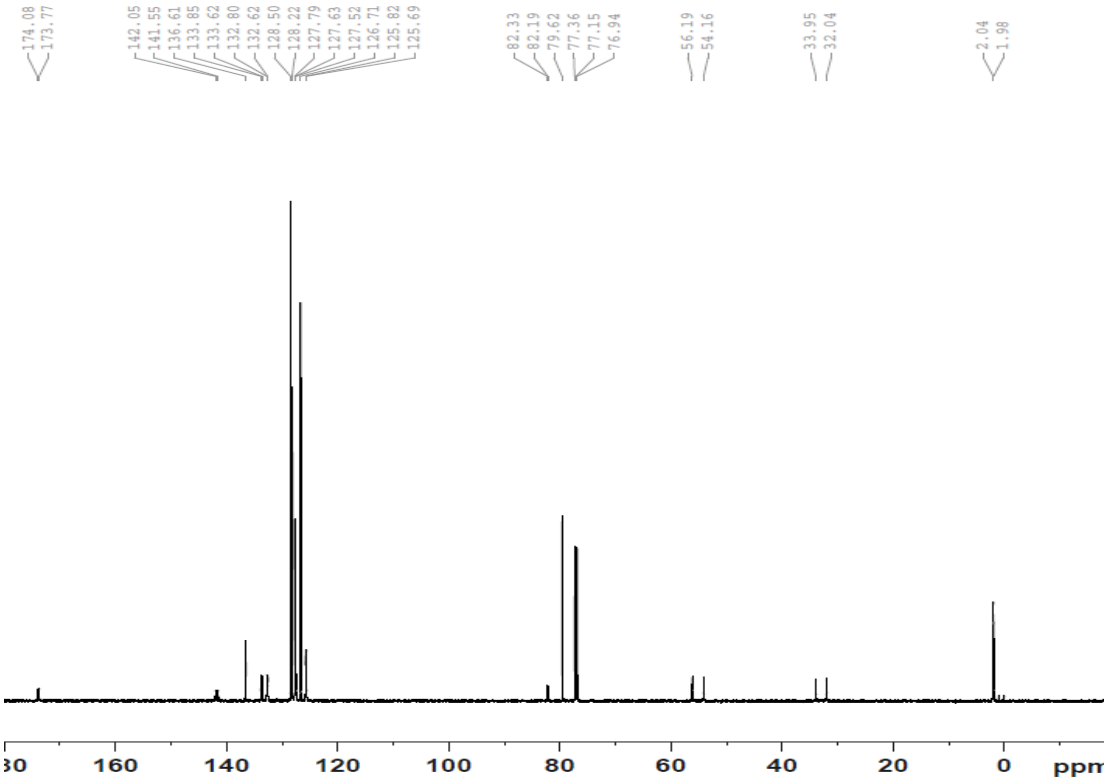


2. ^{13}C NMR spectra of 3a-i (^{13}C NMR (151 MHz) spectra were recorded on a Bruker AR600 MHz spectrometer in $CDCl_3$, with TMS as an internal standard).

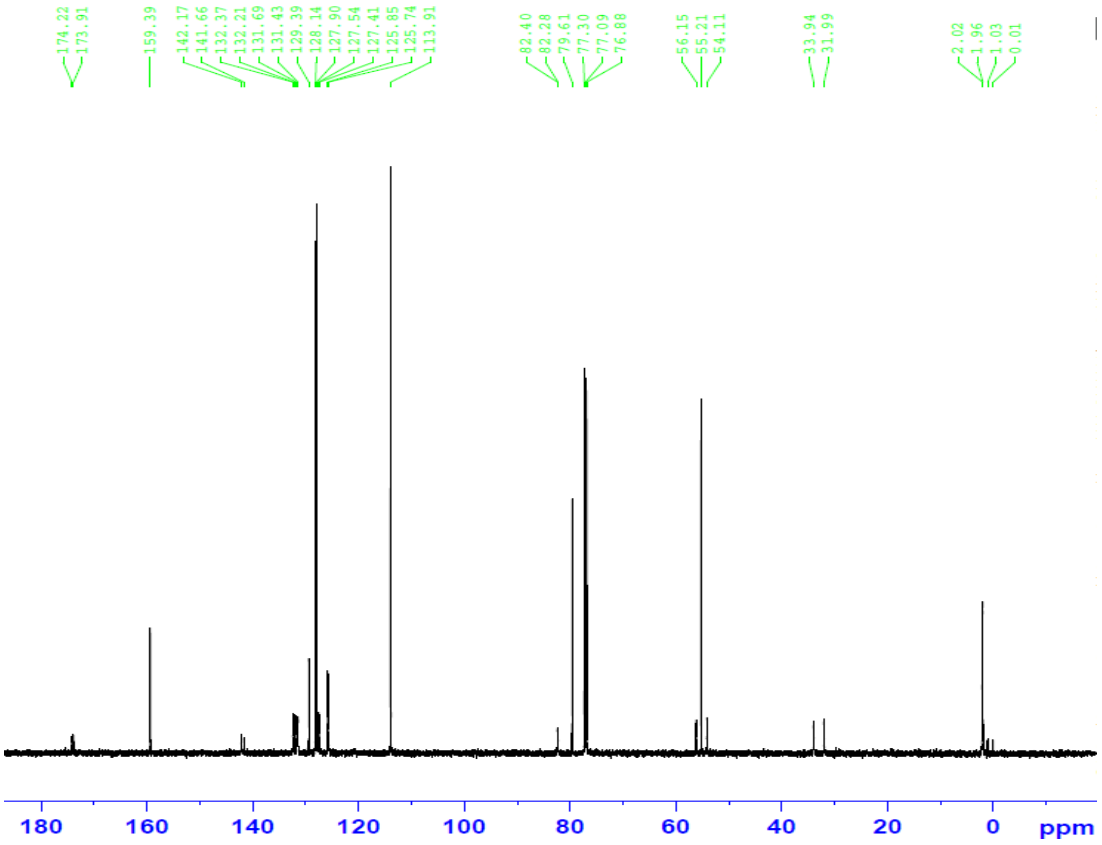
^{13}C NMR of **3a**



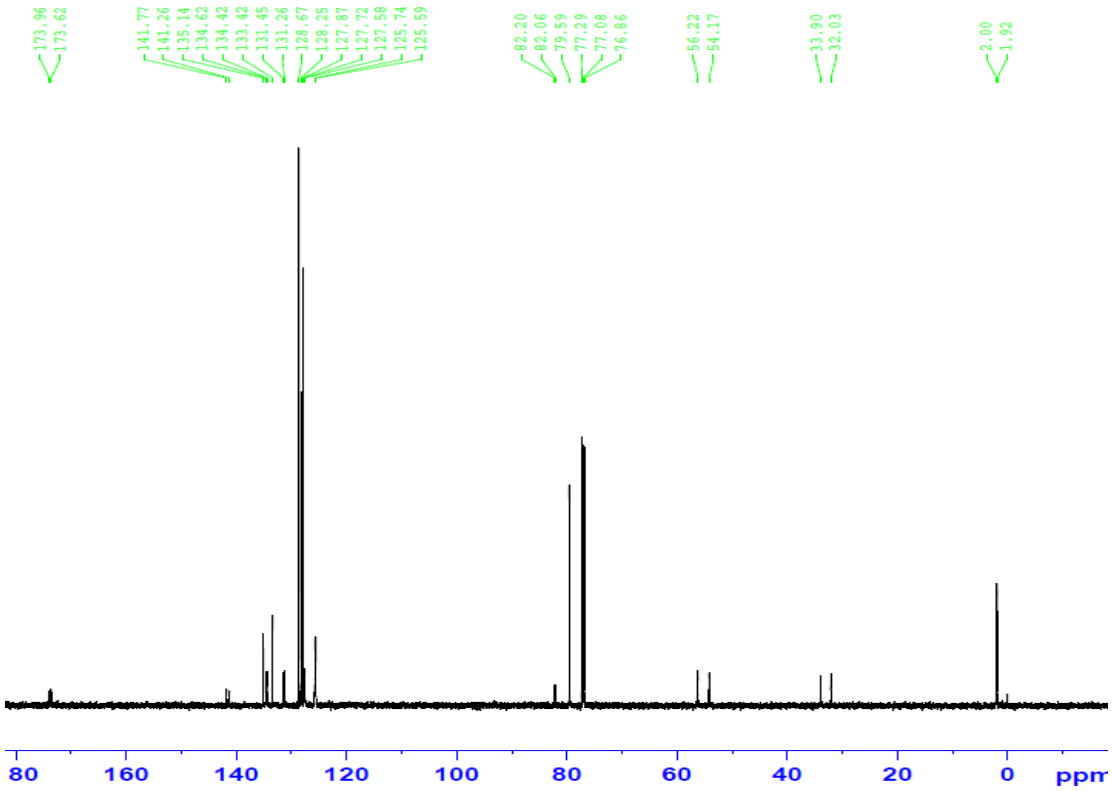
^{13}C NMR of **3b**



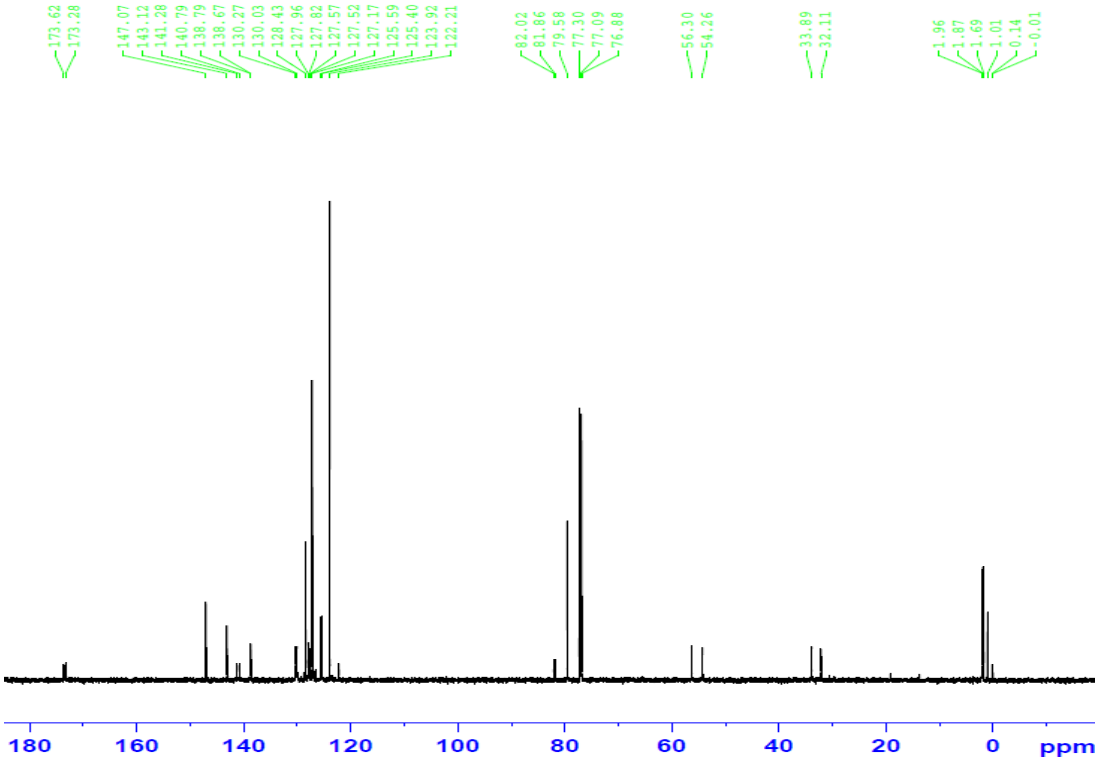
^{13}C NMR of **3c**



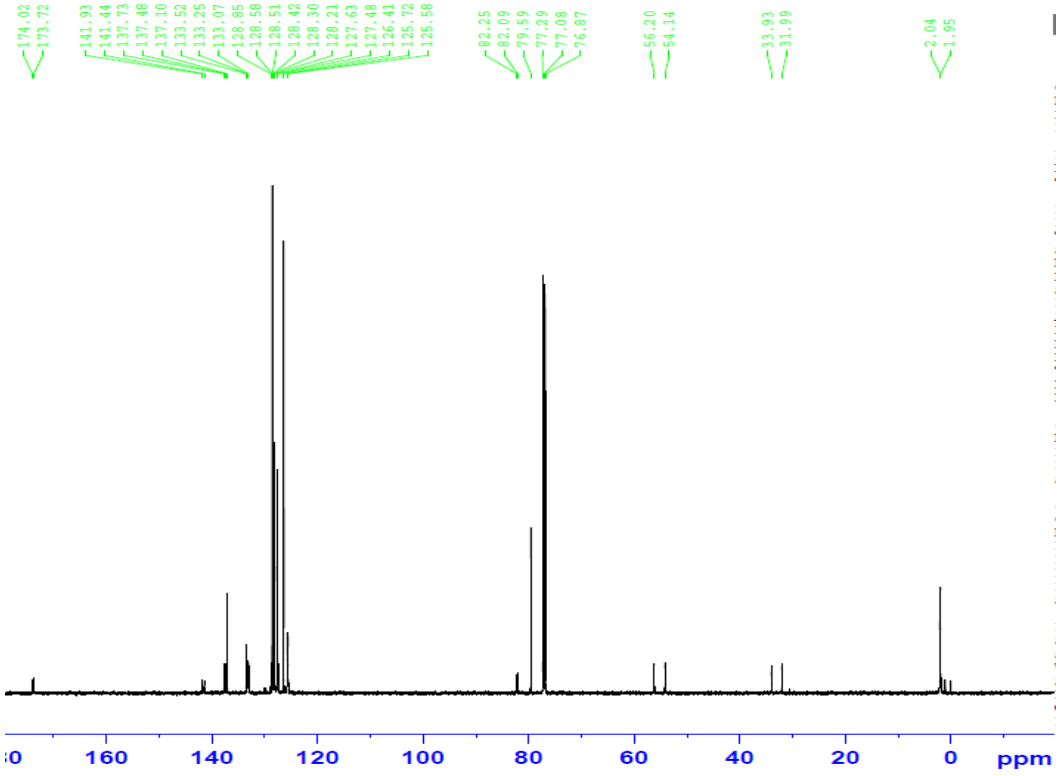
^{13}C NMR of **3d**



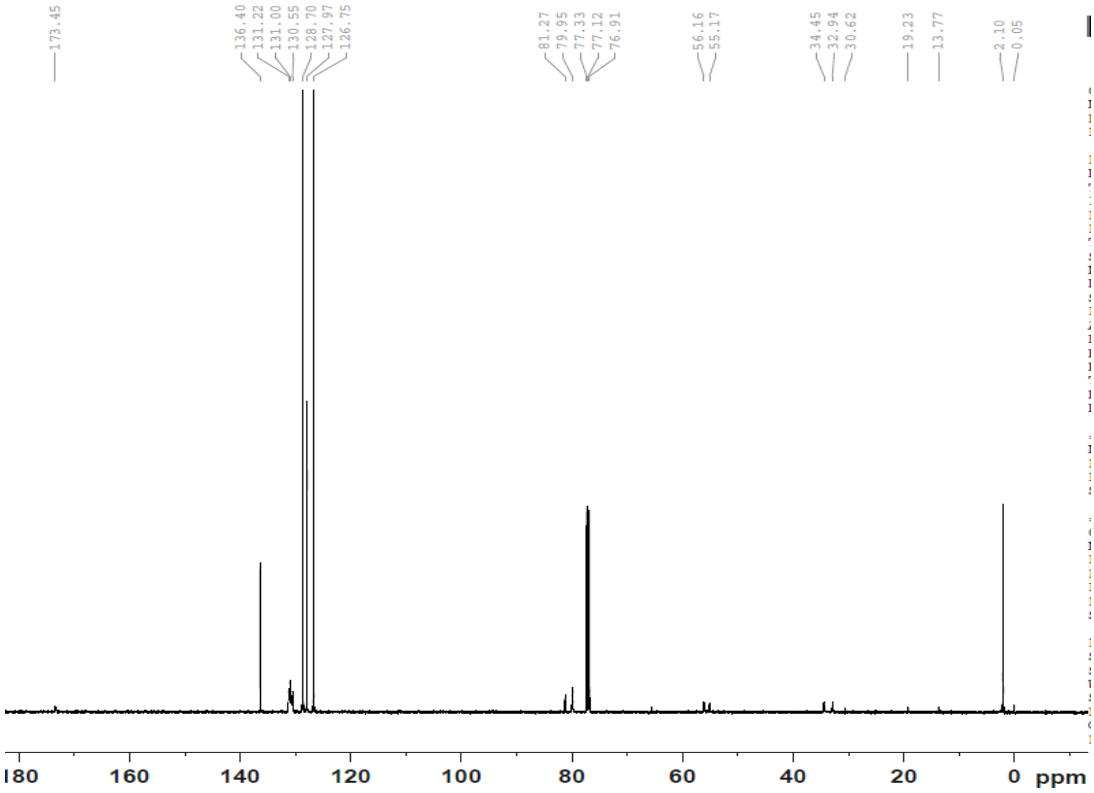
^{13}C NMR of **3e**



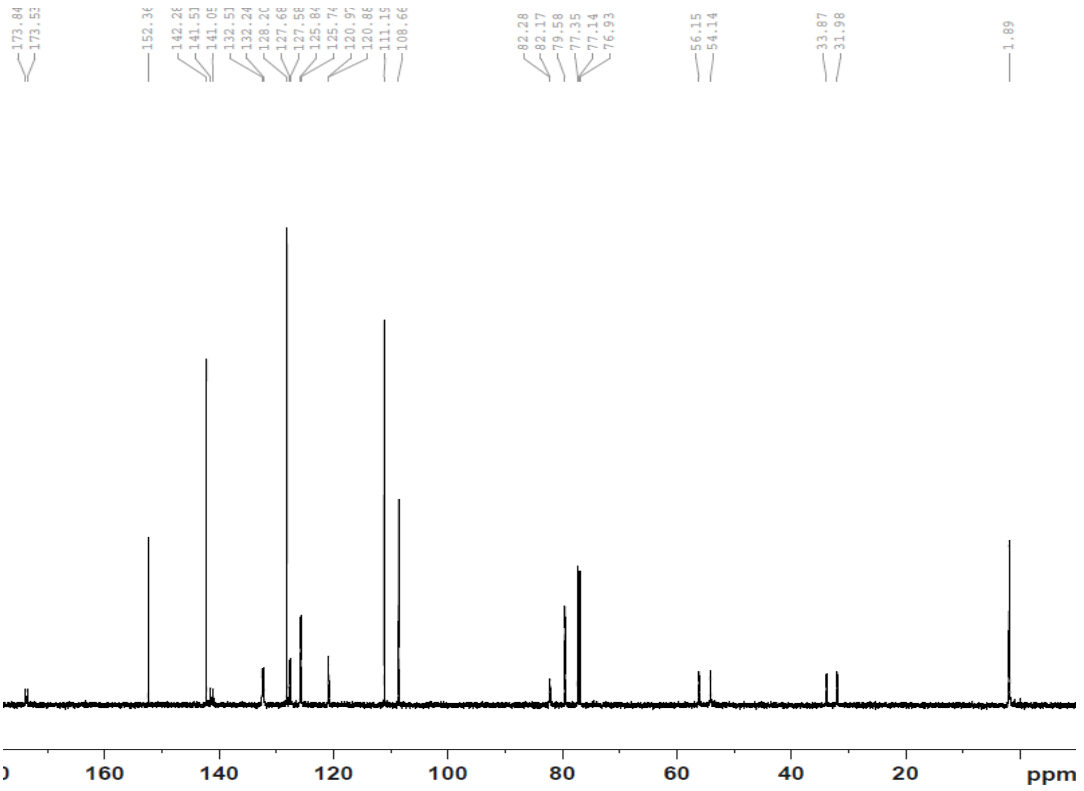
^{13}C NMR of **3f**



^{13}C NMR of **3g**



^{13}C NMR of **3h**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77.35
77.14
76.93
56.15
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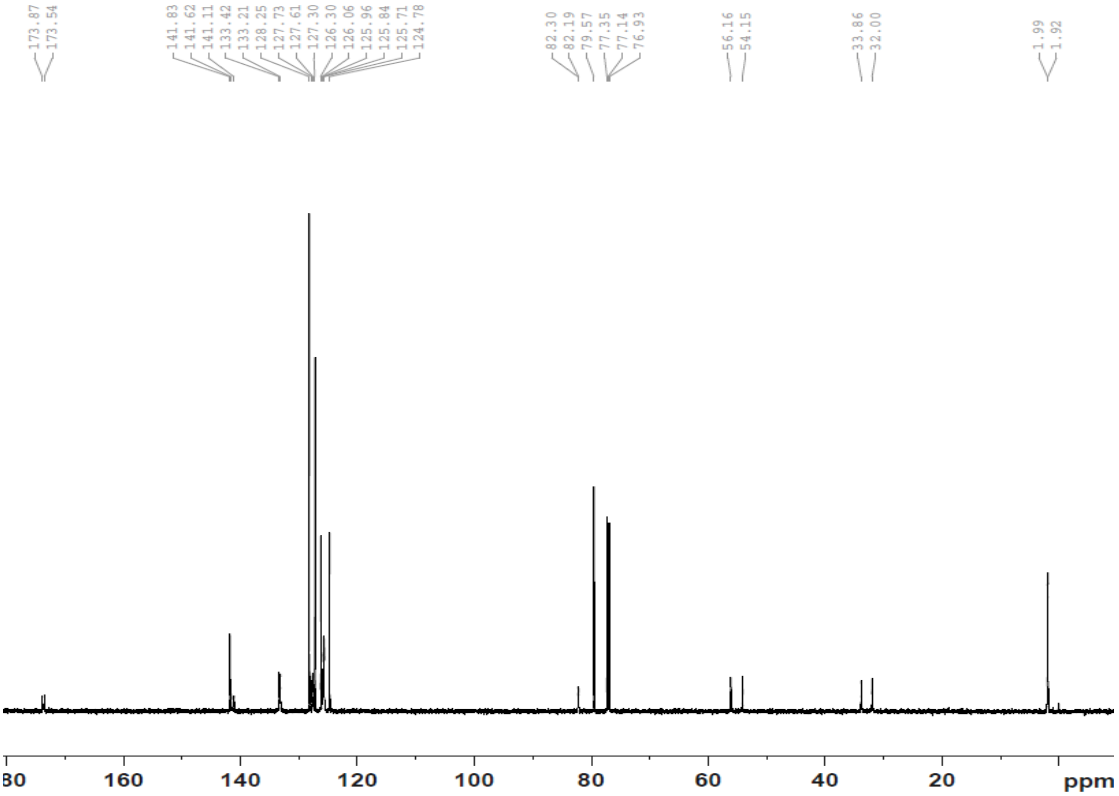
ppm

^{13}C NMR of **3i**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60
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20
ppm