Electronic Supplementary Information

Synthesis, complexation of 1,2,3-(NH)-triazolylferrocene derivatives and their catalytic effect on thermal decomposition of ammonium perchlorate

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Experimental

Materials

Ferrocenylethyne[1] and acyl chloride **1a-f**[2] were prepared according to the reported procedures. Triethylamine and CH_2Cl_2 were distilled from calcium hydride before use. Toluene was dried and distilled from sodium. All other chemicals (AR) obtained from commercial sources were used without further purification.

Measurements

Fourier transform infrared spectroscopy (IR) spectra were recorded as KBr pellets on a NEXUS-670FT spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on an Avance 500 Bruker (500 MHz) spectrometer using tetramethyl silicane as internal standard. The mass spectral analyses were obtained on the LCQ Advantage Max mass spectrometer (ESI resource). Elemental analyses were carried out on a Perkin-Elemer-2400 apparatus.

DTA study and TG analysis were performed with a simultaneous DSC/DTA-TGA thermal analyzer, TA SDT Q600. Sample weight was set around 5–6 mg. A heating rate of 10 ºC min^{-1} from 50 to 500 ºC was used for each run. All DTA and TG experiments were conducted with a nitrogen flow rate of 100 mL min^{-1}. The procedure of simply mixing **3a–3c** and AP was as follows: 5% (mass percent) of catalyst was ground with AP in some ethyl alcohol in an agate mortar, and then dried under vacuum at room temperature.

General procedure for the synthesis of ferrocenyl 1,2,3-triazoles 3a-f.

A round-bottom sidearm flask (10 mL) containing $PdCl_2(PPh_3)_2$ (0.02 g, 0.03 mmol), CuI (0.0145 g, 0.075 mmol) and ferrocenylethyne (0.315 g, 1.5 mmol) was subjected to the Schlenk-line procedures of evacuation and purging of N_2 for three cycles. Acyl chloride **1** (2.25 mmol), Et_3N (0.32 mL, 2.25 mmol) and toluene (10 mL) was successively added, and the reaction mixture was stirred at room temperature until ferrocenylethyne disappeared by TLC test, then extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was subjected to flash column chromatography with petroleum ether/EtOAc (10:1, V:V) as eluent, and the second fraction was the crude ynones **2a-f** used the next reaction without further purification.

The crude ynones **2** (about 0.19 mmol), NaN_3 (0.19 g, 0.285 mmol), CuI (1.8 mg, 0.01 mmol) and DMSO (3 mL) were successively added to a round-bottom sidearm flask reacted at r.t. under N_2 until ynones disappeared by TLC test, then extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was subjected to flash column chromatography with petroleum ether/EtOAc (5:1, V:V) as eluent, collecting the second fraction. The solvent was removed by a rotary evaporator to give the desired **3**.

(4-Methoxyphenyl)(5-ferrocenyl-2H-1,2,3-triazol-4-yl)methanone (**3a**)

Yellow crystals, yield, 87%, m.p. 78-80 ºC; ^1H NMR (500 MHz, D^6-DMSO) $\delta = 3.88$ (s, 3H), 4.03 (s, 5H), 4.45 (s, 2H), 5.05 (s, 2H), 7.10 (d, $J = 7.8$ Hz, 2H), 8.10 (d, $J = 7.8$ Hz, 2H), 15.65 (s, 1H) ppm; ^{13}C NMR

(500 MHz, D^6-DMSO) δ = 185.97, 170.32, 163.24, 140.63, 132.56, 130.34, 113.73, 69.58, 69.48, 68.97, 55.57 ppm; IR (KBr, ν_{max}):3410, 3230, 3150, 3112, 3007, 1645, 1597, 1459, 1261, 1167, 1088, 1025, 920, 843, 623, 503 cm^{-1}; ESI-MS *m/z*: calcd for [M + H]$^+$ 388.07, found: 388.03; Anal. calcd for $C_{20}H_{17}FeN_3O_2$: C, 62.04; H, 4.43; N, 10.85; Found: C, 62.12; H, 4.49; N, 10.64.

(4-Nitrophenyl)(5-ferrocenyl-2H-1,2,3-triazol-4-yl)methanone (**3b**)

Black-red crystals, yield, 56%, m.p. 164-166 ºC; ^{1}H NMR (500 MHz, D^6-DMSO) δ = 4.11 (s, 5H), 4.55 (s, 2H), 5.20 (s, 2H), 8.28 (d, *J* = 7.0 Hz, 2H), 8.39 (d, *J* = 7.0 Hz, 2H), 15.87 (s, 1H) ppm; ^{13}C NMR (500 MHz, D^6-DMSO) δ = 185.81, 149.46, 143.28, 139.63, 131.28, 123.32, 70.16, 69.71, 69.36 ppm; IR (KBr, ν_{max}): 3416, 3152, 3095, 2990, 1655, 1600, 1522, 1449, 1347, 1266, 1173, 1107, 1043, 1004, 918, 846, 706, 509 cm^{-1}; ESI-MS *m/z*: calcd for [M + H]$^+$ 403.05, found: 403.06; Anal. calcd. for $C_{19}H_{14}FeN_4O_3$: C, 56.74; H, 3.51; N, 13.93; Found: C, 56.52; H, 3.75; N, 13.73.

(4-Bromophenyl)(5-ferrocenyl-2*H*-1,2,3-triazol-4-yl)methanone (3c)

Yellow crystals, yield, 64%, m.p. 168-170 ºC; ^{1}H NMR (500 MHz, D^6-DMSO) δ = 4.08 (s, 5H), 4.50 (s, 2H), 5.17(s, 2H), 7.80 (d, *J* = 7.4 Hz, 2H), 8.06 (d, *J* = 7.4 Hz, 2H), 15.79 (s, 1H) ppm; ^{13}C NMR (500 MHz, D^6-DMSO): δ = 186.12, 170.28, 139.98, 136.90, 132.11, 131.39, 127.02, 69.90, 69.61, 69.24 ppm; IR (KBr, ν_{max}):3431, 3150, 3087, 2997, 1649, 1583, 1457, 1268, 1175, 1111, 1069, 1006, 916, 821, 627, 512 cm^{-1}; ESI-MS *m/z*: calcd for [M + H]$^+$ 435.97, [M + H + 2]$^+$ 437.96, found: 435.98 (100%), 437.96 (94%); Anal. Calcd for $C_{19}H_{14}BrFeN_3O$: C, 52.33; H, 3.24; N, 9.64; Found: C, 52.09; H, 3.57; N, 9.91.

Furan-2-yl(5-ferrocenyl-2*H*-1,2,3-triazol-4-yl)methanone (**3d**)

Orange crystals, yield, 80%, m.p. 184-186 ºC; ^{1}H NMR (500 MHz, D^6-DMSO) δ = 4.07 (s, 5H), 4.50 (s, 2H), 5.15 (s, 2H), 6.80 (q, 1H), 7.88 (s, 1H), 8.13 (s, 1H), 15.73 (s, 1H) ppm; ^{13}C NMR (500 MHz, D^6-DMSO) δ = 173.06, 151.38, 148.41, 139.37, 139.35, 122.31, 112.67, 69.83, 69.56 69.24 ppm; IR (KBr, ν_{max}): 3202, 3141, 3088, 1627, 1563, 1470, 1230, 1086, 1026, 1005, 945, 890, 818, 760, 502 cm^{-1}; ESI-MS *m/z*: calcd for [M + H]$^+$ 348.04, found: 348.06; Anal. calcd for $C_{17}H_{13}FeN_3O_2$: C, 58.82; H, 3.77; N, 12.10; Found: C, 58.53; H, 3.80; N, 12.05.

(3,5-Dinitrophenyl)(5-ferrocenyl-2H-1,2,3-triazol-4-yl)methanone (**3e**)

Black-red crystals, yield, 50%, m.p. 98-100 ºC; ^{1}H NMR (500 MHz, D^6-DMSO) δ = 4.15 (s, 5H), 4.58 (s, 2H), 5.25 (s, 2H), 9.06 (s, 1H), 9.28 (s, 2H), 16.01 (s, 1H) ppm; ^{13}C NMR (500 MHz, D^6-DMSO) δ = 181.99, 147.90, 140.25, 139.07, 130.09, 121.60, 70.34, 69.81, 69.47 ppm; IR (KBr, ν_{max}): 3245, 3106, 2995, 1715, 1662, 1541, 1466, 1344, 1265, 1117, 1047, 920, 826, 731, 511 cm^{-1}; ESI-MS *m/z*: calcd for M$^+$ 447.03, found: 447.20; Anal Calcd for $C_{19}H_{13}FeN_5O_5$: C, 51.03; H, 2.93; N, 15.66; Found: C, 51.31; H, 3.12; N, 15.46.

(6-ethoxynaphthalen-2-yl)(5-ferrocenyl-2*H*-1,2,3-triazol-4-yl)methanone (**3f**)

Orange crystals, yield, 64%, m.p. 80-82 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.46 (t, *J* = 6.7 Hz, 3H), 4.02 (s, 5H), 4.12 (q, *J* = 6.7 Hz, 2H), 4.31 (s, 2H), 5.09 (s, 2H), 7.11 (s, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.67 (s, 1H), 14.45 (s, 1H) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ = 187.47, 159.31, 144.32, 140.93, 137.51, 133.11, 132.88, 131.55, 127.67, 127.00, 126.28, 119.88, 106.46, 70.38, 70.03, 69.57, 63.69, 14.76 ppm; IR (KBr, ν_{max}): 3250, 3102, 2979, 2850, 1621, 1471, 1266, 1176, 1111, 1042, 1000, 916, 818, 626, 506 cm^{-1}; ESI-MS *m/z*: calcd for M$^+$ 451.10, found: 451.08; Anal. calcd for $C_{25}H_{21}FeN_3O_2$: C, 66.53; H, 4.69; N, 9.31; Found: C, 66.39; H, 4.43; N, 9.12.

General procedure for the synthesis of complexes

To a solution of **3a-d** (100 mg, 0.19 mmol) in dry ethanol (16 mL), the solution of NaOH (1 mL, 0.25 M) was added in order to adjust the pH of solution (about 8-9) and stirred under reflux, then the hot solution of

$M(OAc)_2·H_2O$ (0.19 mmol) in ethanol (15 mL) was added dropwise to the stirred solution. The mixture was refluxed under stirring for 8 h until the precipitates were no more separated. The precipitates were isolated by centrifugation, washed several times with distilled water and anhydrous ethanol, filtered to give the corresponding complexes

(**3a**)Cu(OAc), khaki powder, yield, 70%; IR (KBr, ν_{max}): 3115, 2970, 2924, 1644, 1564, 1467, 1225, 1157, 1104, 1024, 951, 855, 823, 594, 505 cm^{-1}; Anal. Calcd for $C_{22}H_{19}CuFeN_3O_4$: C, 51.93; H, 3.76; N, 8.26; Found: C, 51.66; H, 3.80; N, 7.98.

(**3a**)Zn(OAc), orange powder, yield, 74%; IR (KBr, ν_{max}): 3093, 2902, 2840, 1640, 1598, 1458, 1260, 1165, 1024, 1088, 1024, 920, 838, 622, 503 cm^{-1}; Anal. Calcd for $C_{22}H_{19}FeN_3O_4Zn$: C, 51.74; H, 3.75; N, 8.23; Found: C, 51.55; H, 3.52; N, 8.47.

(**3b**)Cu(OAc)(H_2O), khaki powder, yield, 58%; IR (KBr, ν_{max}): 3097, 1665, 1601, 1525, 1445, 1345, 1178, 1103, 922, 846, 701, 483 cm^{-1}; Anal. Calcd for $C_{21}H_{18}CuFeN_4O_6$: C, 46.55; H, 3.35; N, 10.34; Found: C, 46.53; H, 3.60; N, 10.05.

(**3b**)Zn(OAc), orange powder, yield, 62%; IR (KBr, ν_{max}): 3101, 1787, 1659, 1602, 1526, 1445, 1347, 1168, 1104, 919, 849, 708, 483 cm^{-1}; Anal. Calcd for $C_{21}H_{16}FeN_4O_5Zn$: C, 47.99; H, 3.07; N, 10.66; Found: C, 47.73; H, 3.27; N, 10.70.

(**3c**)Cu(OAc), khaki powder, yield, 64%; IR (KBr, ν_{max}): 3091, 1659, 1448, 1276, 1169, 1104, 1067, 1007, 918, 819, 506, 486 cm^{-1}; Anal. Calcd for $C_{21}H_{16}BrCuFeN_3O_3$: C, 45.23; H, 2.89; N, 7.54; Found: C, 45.42; H, 2.73; N, 7.76.

(**3c**)Zn(OAc)(H_2O), orange powder, yield, 68%; IR (KBr, ν_{max}): 3093, 1658, 1584, 1449, 1284, 1173, 1103, 1069, 1009, 922, 823, 505 cm^{-1}; Anal. Calcd for $C_{21}H_{18}BrFeN_3O_4Zn$: C, 43.67; H, 3.14; N, 7.28; Found: C, 43.41; H, 3.25; N, 6.99.

(**3d**)Cu(OAc), khaki powder, yield, 75%; IR (KBr, ν_{max}): 3114, 2964, 1645, 1564, 1466, 1290, 1157, 1102, 1023, 950, 855,766, 594, 505 cm^{-1}; Anal. Calcd for $C_{19}H_{15}CuFeN_3O_4$: C, 48.69; H, 3.23; N, 8.96; Found: C, 48.47; H, 2.98; N, 8.75.

(**3d**)Zn(OAc), orange powder, yield, 78%; IR (KBr, ν_{max}): 3142, 3088, 1630, 1563, 1463, 1283, 1153, 1087, 1028, 854, 759, 626, 502, 464 cm^{-1}; Anal. Calcd for $C_{19}H_{15}FeN_3O_4Zn$: C, 48.49; H, 3.21; N, 8.93; Found: C, 48.28; H, 2.97; N, 8.74.

X-ray crystallography

Data were collected on a Bruker Smart APEX II CCD area detector with a MoK*α* radiation (λ = 0.71073 Å) at 296 K in the φ–ω scan mode. The structure was determined by direct method (SHELXS-97) and successive Fourier synthesis and refined by using the SHELXL-97 program. The nonhydrogen atoms were refined anisotropically, whereas the hydrogen atoms were placed in calculated positions and refined isotropically. Red single crystal of **3d**, suitable for X-ray diffraction analysis, was grown by slow diffusion of petroleum ether into a solution of **3d** in CH_2Cl_2 for about 2 weeks. Crystal data and structure refinement parameters are listed in Table 1. Selected bond distances and angles are given in Table 2.

Reference

1 M. Rosenblum, N. Brawn, J. Papenmeier, *J. Organomet. Chem*. 1966, **6**, 173.

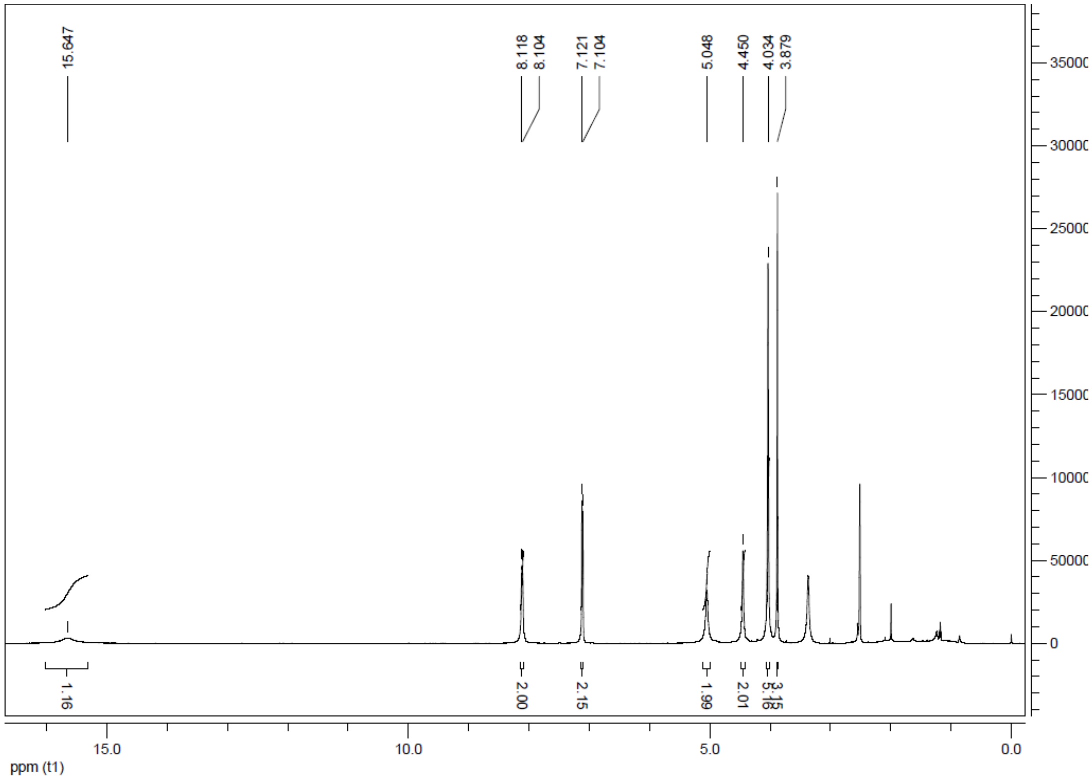
2 Q. R. Lv, X. Meng, J. S. Wu, Y. J. Gao, C. L. Li, Q. Q. Zhu and B. H. Chen, *Catal. Commun.*, 2008, **9**, 2127.

Table 1 Crystal data and structure refinement for **3d**

Compound	**3d**
Empirical formula	$C_{17}H_{13}FeN_3O_2$
Formula weight	347.15
T (K)	296(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	15.961(2)
b (Å)	12.6449(16)
c (Å)	7.1365(9)
α (°)	90
β (°)	94.320(2)
γ (°)	90
Volume (Å^3)	1436.2(3)
Z, calc (mg m^{-3})	4, 1.605
Absorption coefficient (mm^{-1})	1.063
F (000)	712
Crystal size (mm^3)	0.2×0.2×0.2
θ range for data collection (°)	2.06-28.40
Reflections collected / unique	10344 / 3608 [$R_{(int)}$ = 0.0188]
Observed reflections [$I > 2\sigma(I)$]	3051
Completeness to θ = 28.40 (%)	99.80
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3608 / 0 / 208
Goodness-of-fit on F^2	0.914
Final R indices [I > 2sigma (I)]	R_1 = 0.0311, wR_2 = 0.1067
R indices (all data)	R_1 = 0.0386, wR_2 = 0.1147
CCDC No	922174

Table 2 Selected bond distances (Å) and angles (°) of **3d**

Bond distances				Bond angles			
Fe(1)−C(1)	2.049(2)	C(11)−C(12)	1.418(2)	C(7)–C(6)–C(11)	128.99(2)	C(16)–C(17)–O(2)	111.14(2)
Fe(1)−C(2)	2.038(2)	C(12)−C(13)	1.467(2)	C(8)–C(6)–C(11)	123.27(1)	C(14)–O(2)–C(17)	106.33(2)
Fe(1)−C(3)	2.040(2)	C(13)−C(14)	1.457(2)	C(6)–C(11)–C(12)	135.10(1)	C(13)–C(12)–N(3)	120.89(1)
Fe(1)−C(4)	2.043(2)	C(11)−N(1)	1.339(2)	C(6)–C(11)–N(1)	117.59(1)	C(11)–C(12)–N(3)	108.85(1)
Fe(1)−C(5)	2.058(2)	C(12)−N(3)	1.349(2)	C(11)–C(12)–C(13)	130.13(1)	C(12)–C(11)–N(1)	107.21(1)
Fe(1)−C(6)	2.051(2)	N(1)−N(2)	1.330(2)	C(12)–C(13)–C(14)	120.56(1)	C(11)–N(1)–N(2)	103.99(1)
Fe(1)−C(7)	2.044(2)	N(2)−N(3)	1.310(2)	C(12)–C(13)–O(1)	119.90(1)	N(1)–N(2)–N(3)	116.94(1)
Fe(1)−C(8)	2.052(2)	O(1)−C(13)	1.229(2)	C(14)–C(13)–O(1)	119.53(1)	C(12)–N(3)–N(2)	103.01(1)
Fe(1)−C(9)	2.055(2)	O(2)−C(14)	1.375(2)	C(13)–C(14)–O(2)	113.75(1)		
Fe(1)−C(10)	2.053(2)	O(2)−C(17)	1.359(2)	C(15)–C(14)–O(2)	109.21(2)		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2.15
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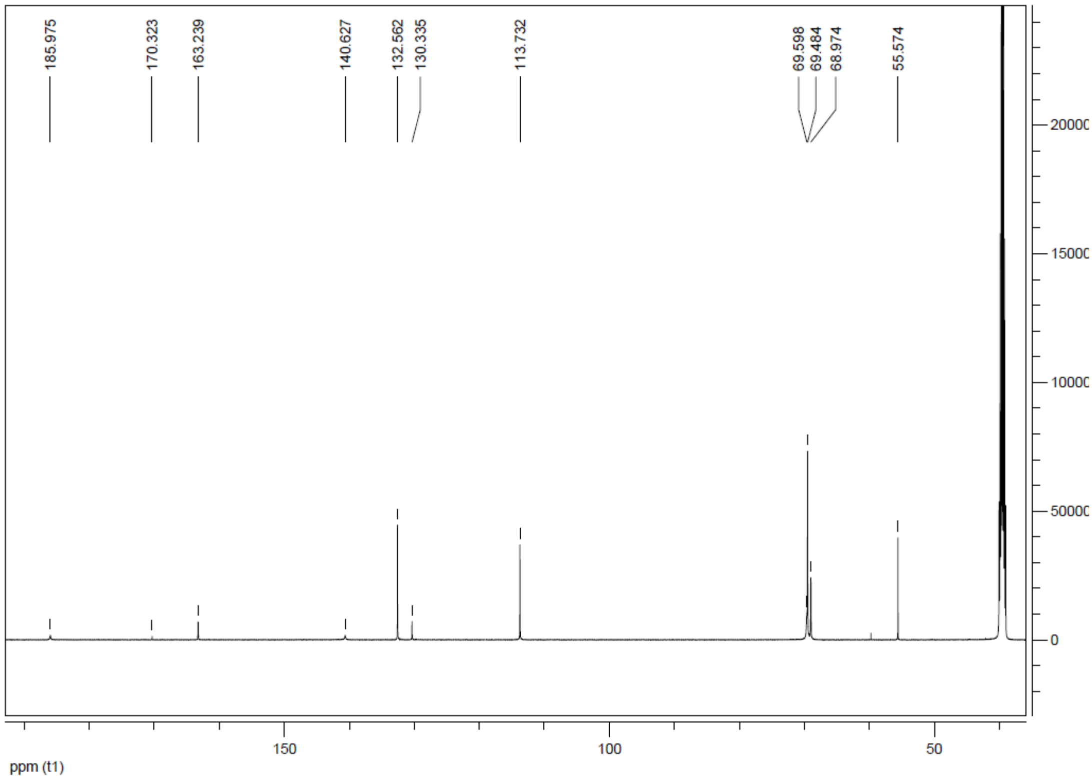
^{1}H NMR of **3a**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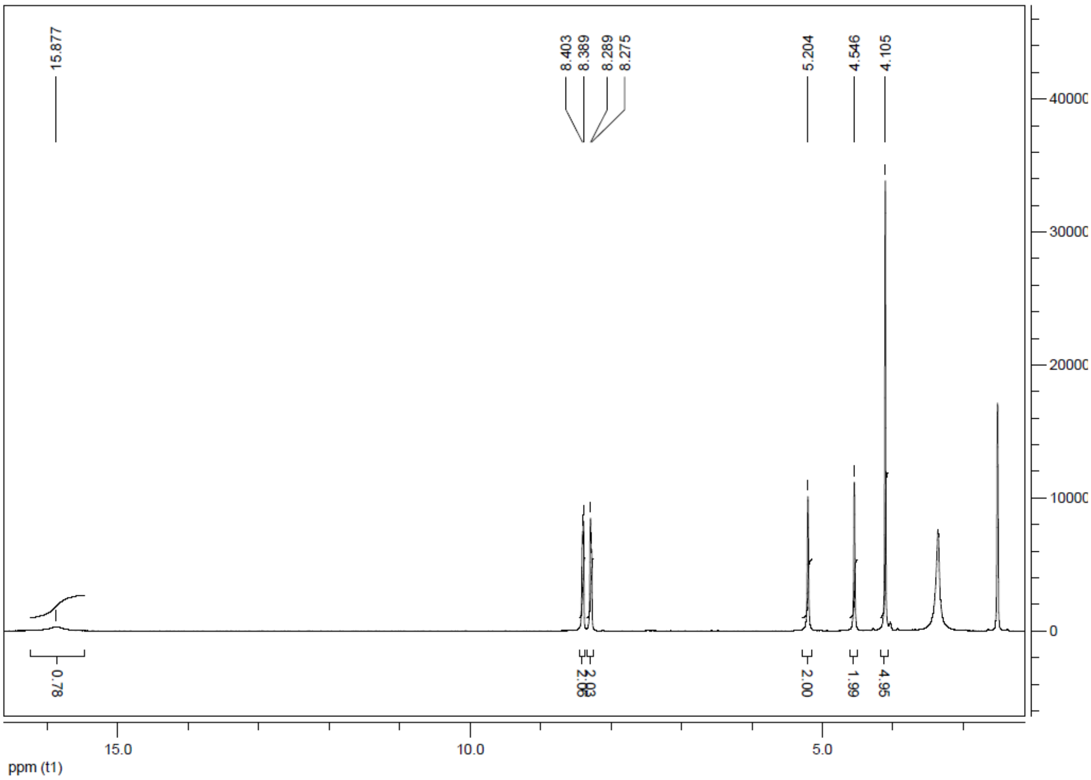
^{13}C NMR of **3a**



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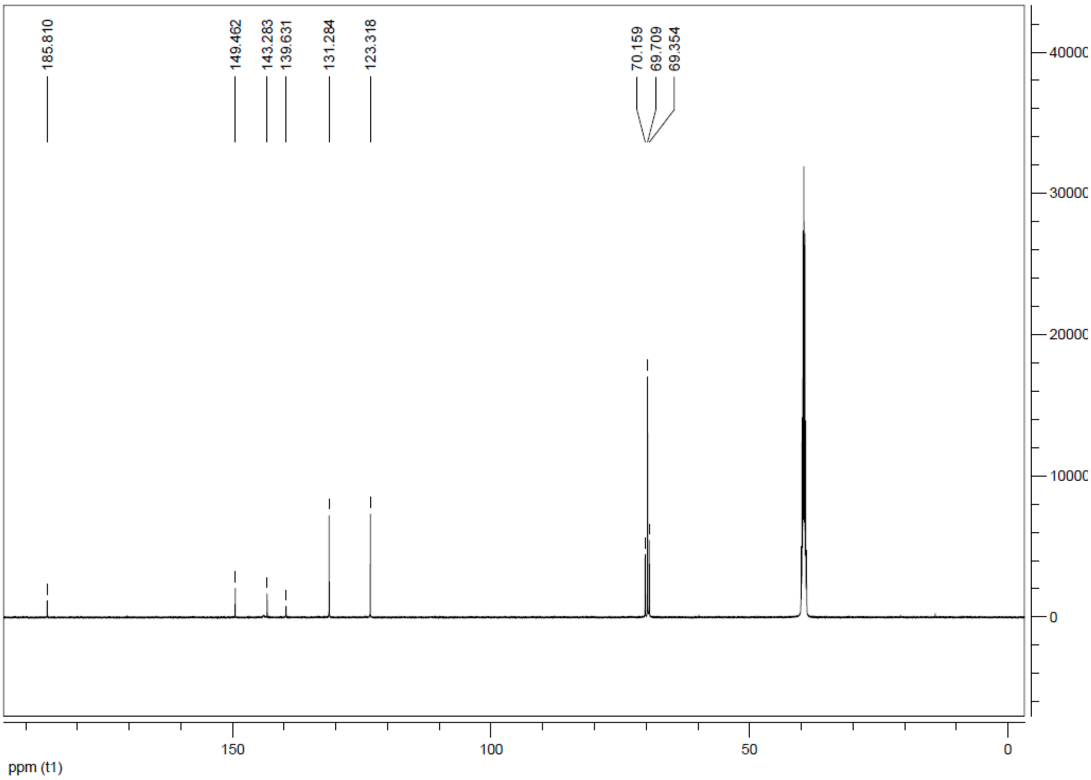

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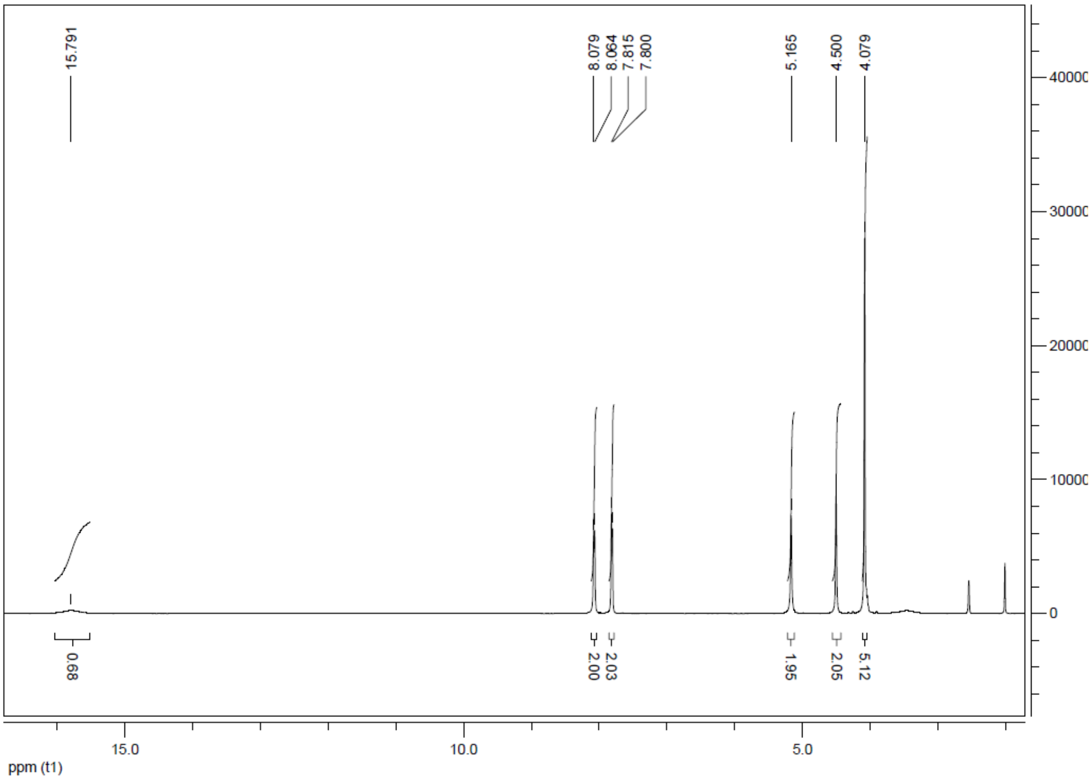

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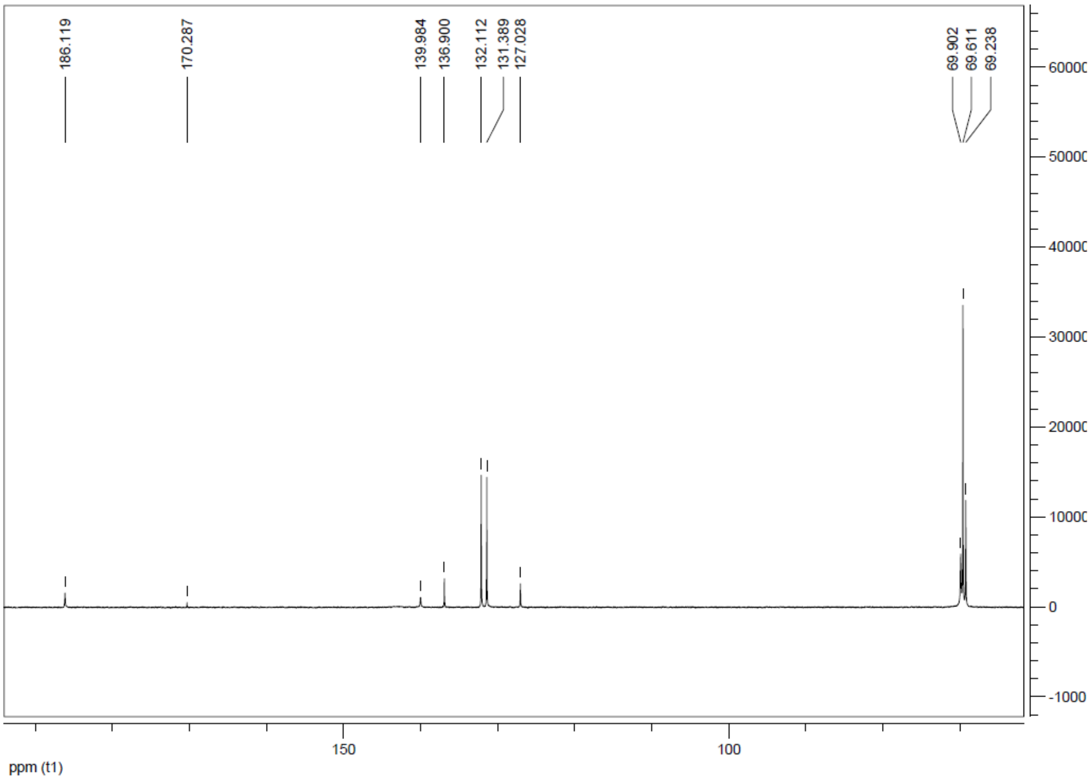

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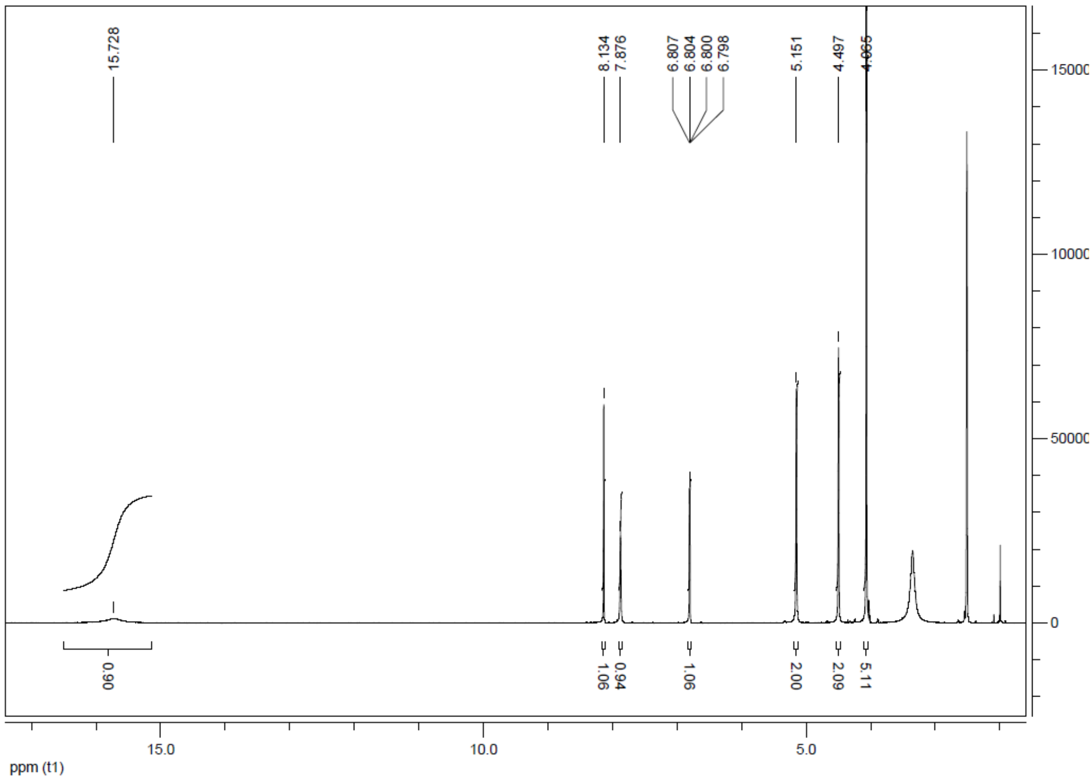

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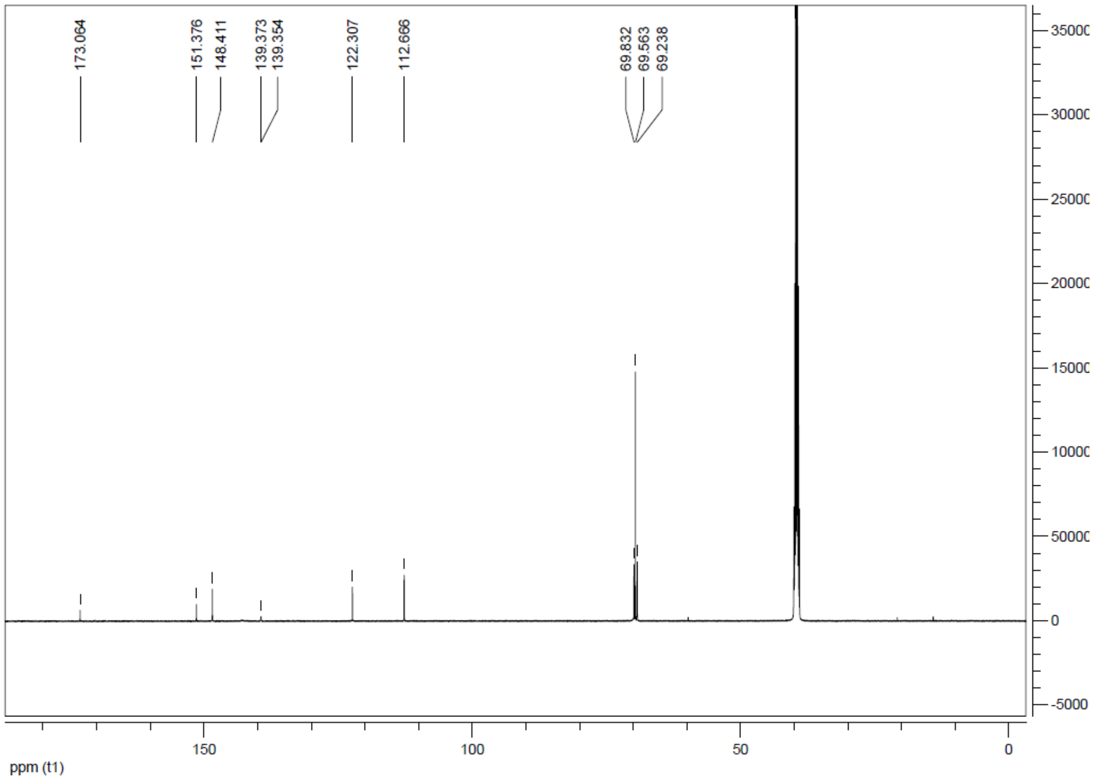

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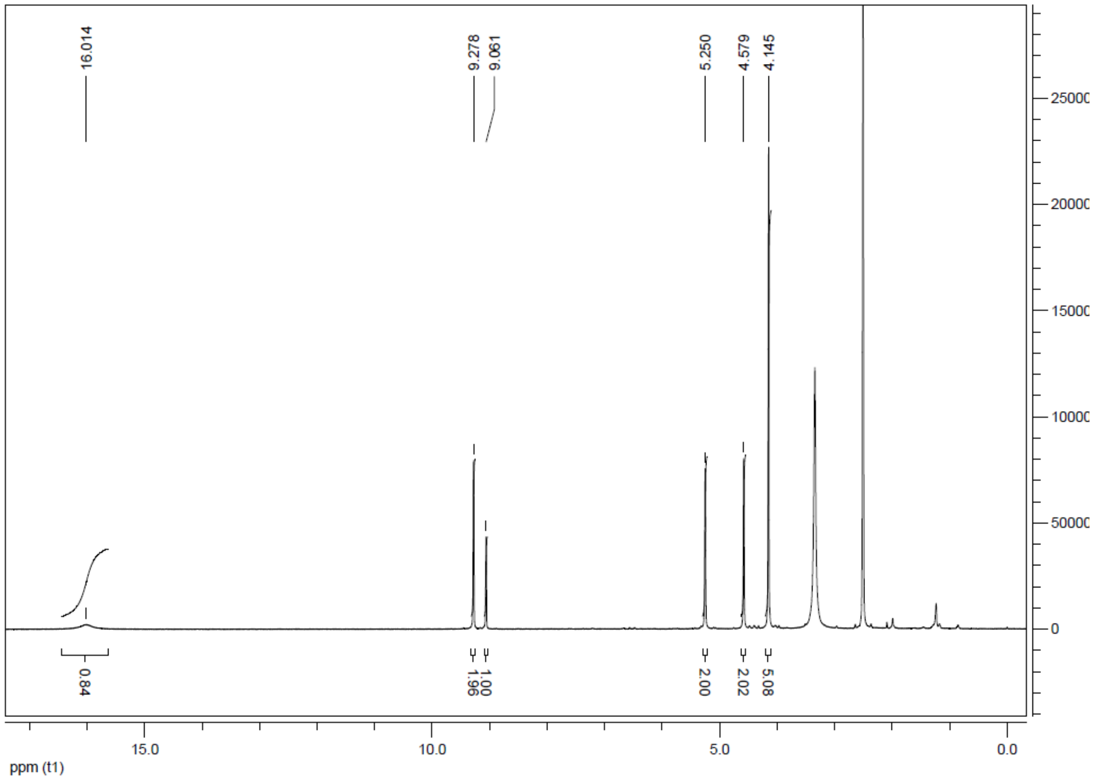

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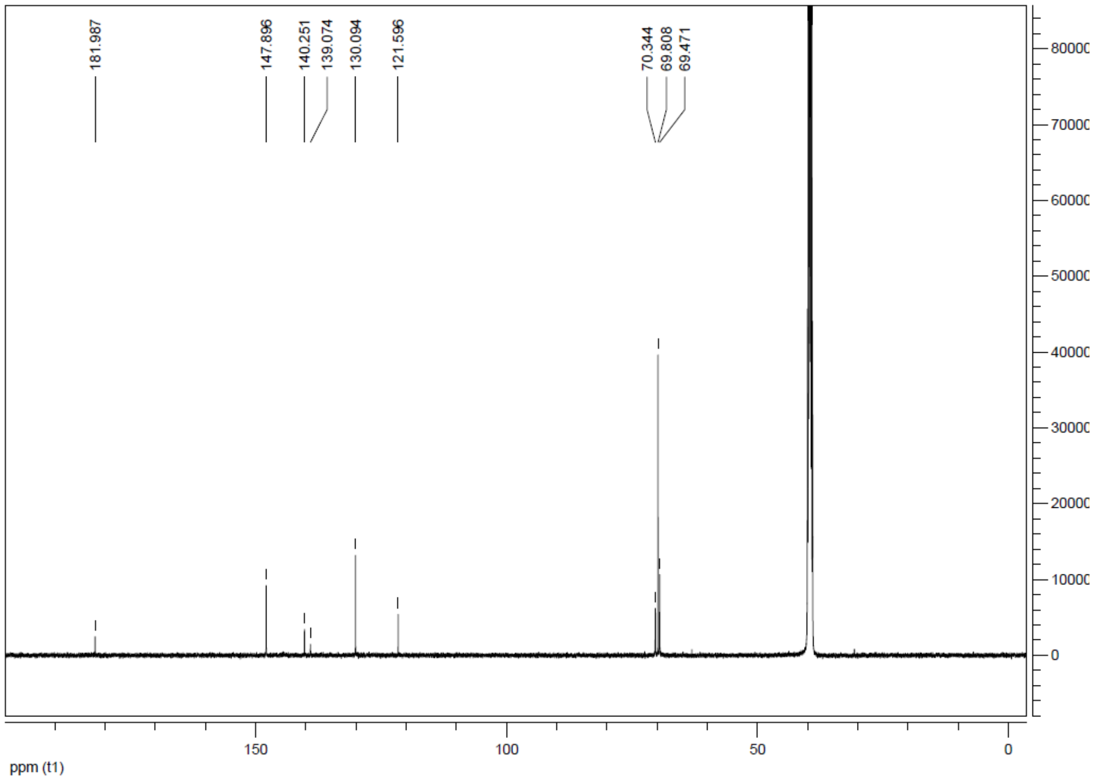
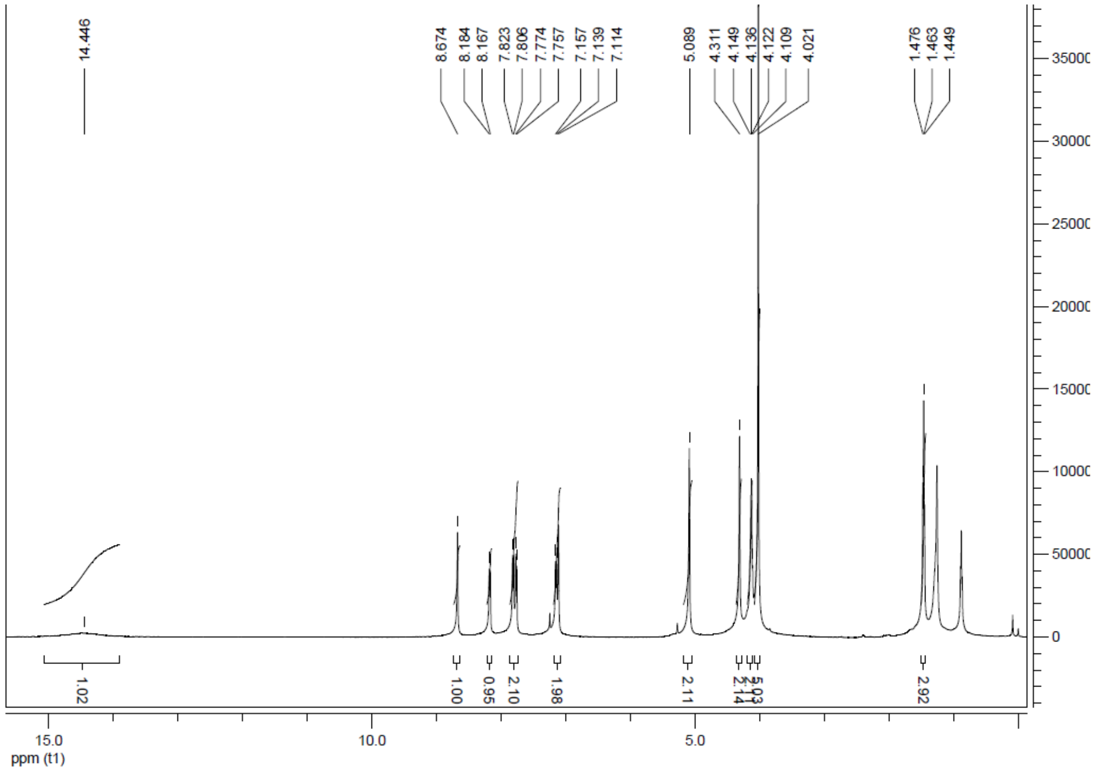
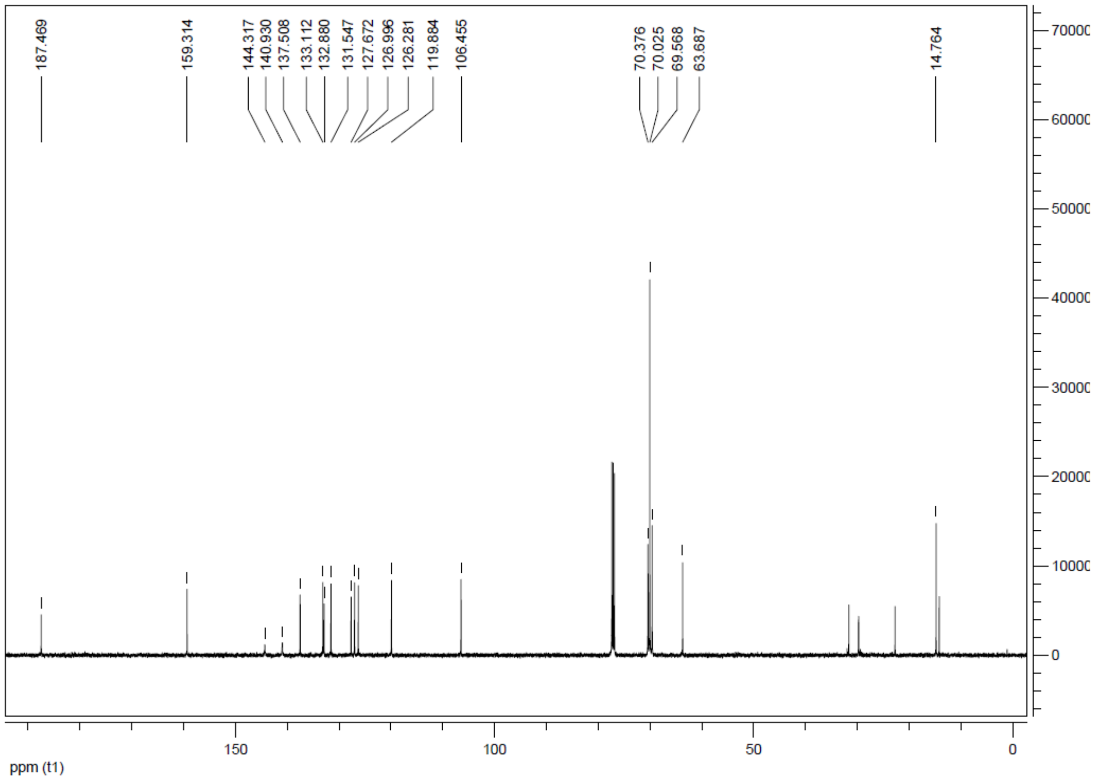


^{13}C NMR of **3e**



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



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