Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

N-Heterocyclic tetracarbene Pd(II) moiety containing Pd(II)-Pb(II) bimetallic MOF for three-component cyclotrimerization via benzyne

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Materials and methods. All chemicals and solvents were at least of analytic grade and employed as received without further purification. The Infrared (IR) spectra were recorded from dry KBr pellets in the 400-4000cm^{-1} range on a PerkinElmer 1600 FTIR spectrometer. The C, H and N elemental analysis were conducted on a PerkinElmer Model 2400 analyzer. Solution phase ^{1}H NMR spectrum was obtained on an AM-300 spectrometer. Chemical shifts are reported in δ units relative to TMS. Powder X-ray diffraction (PXRD) measurements were performed at 293K on a D8 ADVANCE diffractometer (Cu Kα, λ = 1.5406Å). XPS spectra were obtained from PHI Versaprobe II. Thermogravimetric analyses were carried out on a TA Instrument Q5 simultaneous TGA under flowing nitrogen at a heating rate of 10°C/min.

Single-crystal structure determination. Suitable single crystals were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 298(2) K on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, λ = 0.71073 Å). The raw frame data were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[1] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[1] The crystal showed no evidence of crystal decay during data collection. The structure was solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least squares technique. Upon successful solution and refinement in *P-1*. A large void space is present between the framework, which contains many significant electron density peaks. The species in this region were too severely disordered to be modeled, and were treated with SQUEEZE/PLATON. These species include some H_2O molecules. Crystal data, data collection parameters, and refinement statistics are listed in Tables S2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC 1472920. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of Pd(II)-NHDC (A). **A** was synthesized according to the reported method.[2]

Synthesis of Pd(II)-Pb(II)-MOF (B). A mixture of $Pb(NO_3)_2$ (16 mg, 0.04 mmol), **A** (6.8 mg, 0.01 mmol) and $Na_2C_2O_4$ (0.7 mg, 0.005 mmol) in H_2O (1.5 mL) and ethanol (0.5 mL) was sealed in a glass tube. The mixture was heated at 150 °C for 48 h. After the mixture was allowed to cool to room temperature (18 h), colourless crystals of **B** were isolated in 36% yield. FT-IR (KBr pellets, cm^{-1}): 3409 (s), 3157 (s), 3091 (m), 1606 (vs), 1543 (s), 1465 (w), 1382 (vs), 1310 (s), 1176 (w), 1114 (w), 847 (m), 783 (m), 760 (m), 698 (m), 498 (w). Anal. Calcd for $Pb_4PdL_2Br_4(C_2O_4)\cdot 11H_2O$ (**L** = $C_{21}H_{14}N_4O_4$): C, 22.82; H, 2.85; N, 10.89. Found: C, 22.35; H, 2.62; N, 10.47.

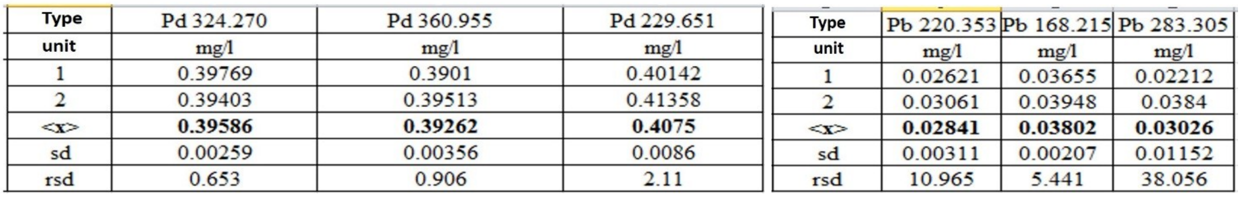
The general catalytic reaction procedure for benzyne cyclotrimerization. The benzyne cyclotrimerization catalysed by **A** or **B** was carried out in an inert atmosphere. A mixture of 2-(trimethylsilyl)phenyl triflate (122 µL, 0.5 mmol), CsF (228 mg, 1.5 mmol), **A** (34 mg, 10 mol % Pd, finely ground) or **B** (11 mg, 1 mol % Pd, finely ground) and

CH_3CN (3 mL) was stirred at 60°C for 2 - 4 h (monitored by TLC) to afford the corresponding triphenylene. The product was purified by the column on silica gel using petroleum ether as the eluent. Yields of triphenylene are 85 (by **A**) and 83 % (by **B**), respectively. It is different from **A**, **B** can be easily recovered by centrifugation. The recovered **B** was washed with double-distilled water (3.0 mL)/ethanol (3.0 mL) (3 times) and dried at 90°C in vacuum for the next run under the same reaction conditions.

The general catalytic reaction procedure for three-component coupling. The catalytic reactions were carried out in an inert atmosphere. A solution of **1** (0.5 mmol), **2** (0.5 mmol) and **3** (0.6 mmol) in CH_3CN (3 mL) was added to a mixture of **A** (34 mg, 10 mol% Pd, finely ground) or **B** (11 mg, 1 mol % Pd, finely ground) and CsF (228 mg, 1.5 mmol). The reaction mixture was stirred at 60°C and monitored by TLC. The substrate of 1 was completely consumed after 4 h. Then, the reaction mixture was poured into water-CH_2Cl_2 (1:1) mixed solvent system (4 mL). The water phase was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered. The solvent was removed in vacuum, and the reside was purified by chromatography on silica gel using petroleum ether as the eluent to give **5** and **4**, respectively. It is different from **A**, **B** can be readily recovered by centrifugation. The recovered **B** was washed with double-distilled water (3.0 mL)/ethanol (3.0 mL) (3 times) and dried at 90°C in vacuum for the next run under the same reaction conditions.

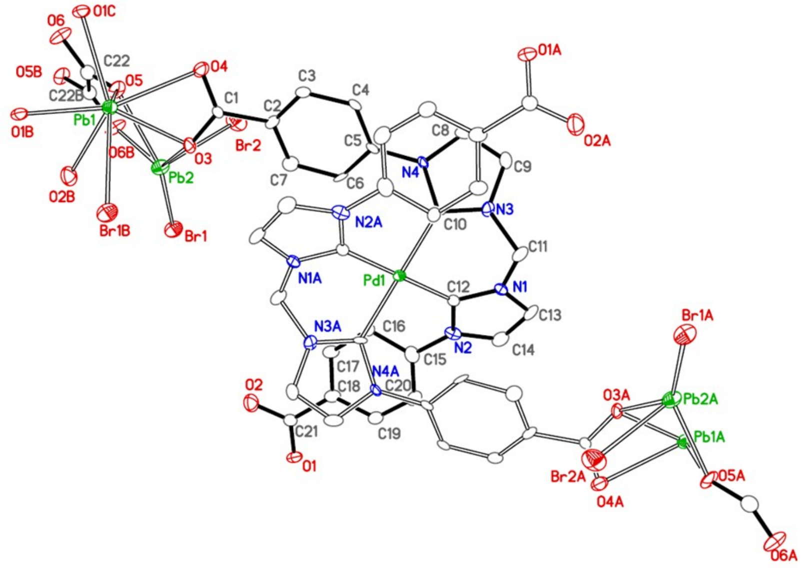
After cyclic catalysis, the reaction solution of CH_3CN was performed ICP measurement after filtration. The result is shown in Table 1. The result indicates that the leaching amount of Pd and Pb is ca. 1.8 and 0.018 %, respectively.

Table S1. ICP result for Pd in the reaction CH_3CN solution after cyclic catalysis



Type	Pd 324.270	Pd 360.955	Pd 229.651
unit	mg/l	mg/l	mg/l
1	0.39769	0.3901	0.40142
2	0.39403	0.39513	0.41358
<x>	**0.39586**	**0.39262**	**0.4075**
sd	0.00259	0.00356	0.0086
rsd	0.653	0.906	2.11

Type	Pb 220.353	Pb 168.215	Pb 283.305
unit	mg/l	mg/l	mg/l
1	0.02621	0.03655	0.02212
2	0.03061	0.03948	0.0384
<x>	**0.02841**	**0.03802**	**0.03026**
sd	0.00311	0.00207	0.01152
rsd	10.965	5.441	38.056



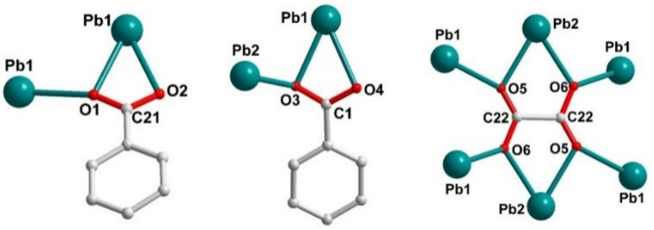


Fig. S1 Top: ORTEP figure of **B**. Bottom: coordination modes of the carboxylate and oxalate groups in **B**. As shown in Fig. S1, the Pd(II) center lies in a square-planar geometry with ligation from four carbenoid carbons which are provided by two metallaligands of **1** (C(10)-Pd(1) = 2.022(17) and C(12)-Pd(1) = 2.025(18) Å). It is different from Pd(II), there are two kinds of crystallographic Pb(II) centres in **B**. Pb(1) adopts a {Pb(1)O$_7$Br} sphere which is composed of five carboxylic oxygen donors from **A** (Pb(1)-O = 2.516 (13) - 2.653(13) Å), two oxygen donors from the oxalate anions (Pb(1)-O = 2.528(13) - 2.630(12) Å) and one weakly coordinated μ-Br$^-$ (Pb(1)-Br(1) = 3.220(3) Å). Pb(2) lies in a {Pb(2)O$_3$Br$_2$} sphere consisting of two chelating oxalate oxygen (O(5) and O(6)), one carboxylate oxygen (O(3)) from **A** and one weakly coordinated μ-Br$^-$ and one terminal coordinated Br$^-$ anions. The Pb(2)-O bond distances are in a range of 2.528(13)-2.566(14) Å, and Pb(2)-Br(1) and Pb(2)-Br(2) bond lengths are 3.076(3) and 2.745(3) Å, respectively.

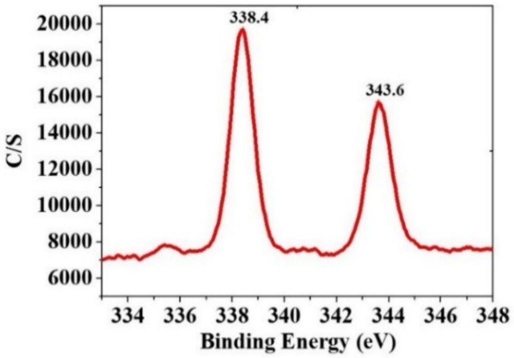


Fig. S2 XPS spectrum of Pd in **B**, indicating that Pd is bivalent.

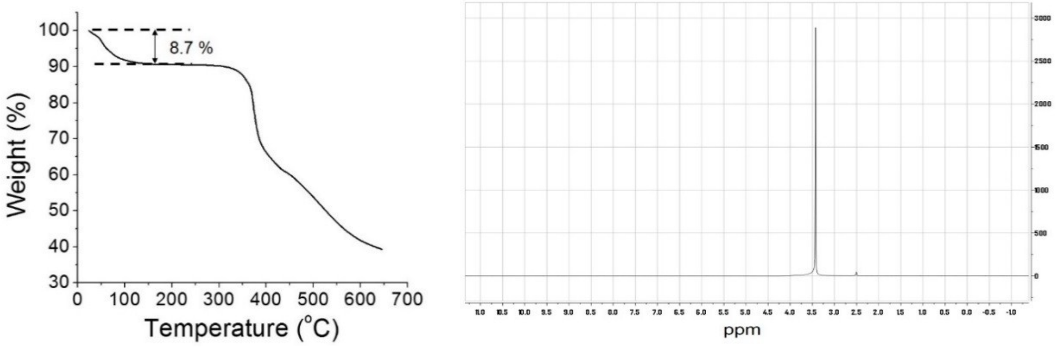


Fig. S3 Left: TGA trace of **$(H_2O)_{11}$⊂Pd(II)-Pb(II)-MOF**. The measured encapsulated guest water content of 8.7 % (calculated 8.5 %) was observed. Right: ^{1}H NMR spectrum of DMSO-d^6 extract confirms that the encapsulated guest solvent is water.

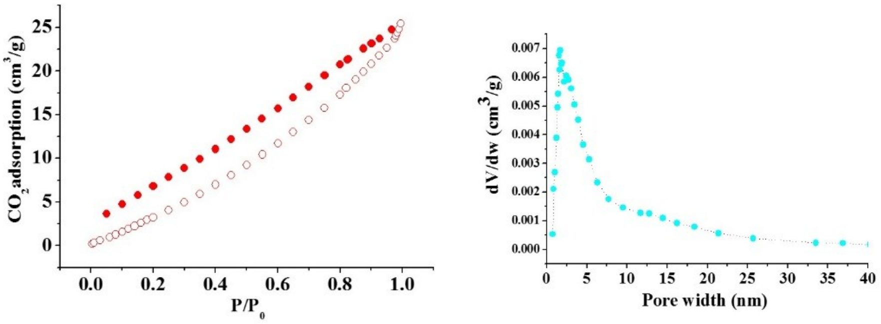


Fig. S4 Left: Left: CO$_2$ sorption isotherms at 195 K of **B (**solid symbols: adsorption, open symbols: desorption). Right: the pore width of **B** is centred at 1.6 nm.

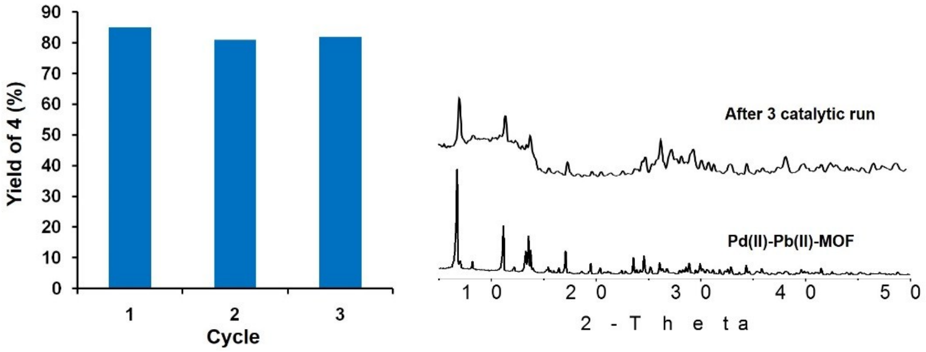


Fig. S5 Left: recycling catalytic test for benzyne cyclotrimerization based on 2-(trimethylsilyl)phenyl trifluoromethanesulfonate catalyzed by **B**. Right: XRPD patterns of **B** and it was used after three catalytic runs.

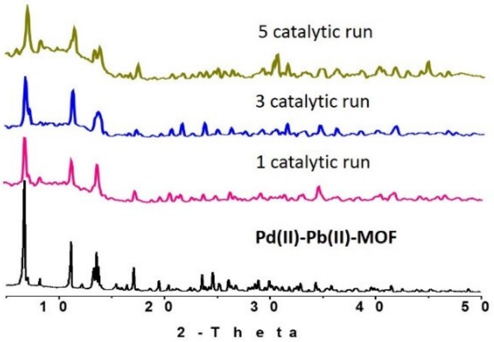


Fig. S6 The XRPD patterns of as-synthesized **B** sample and it was used for three-component coupling reaction after 1, 3 and 5 catalytic runs.

Table S2. Crystal data of **B**

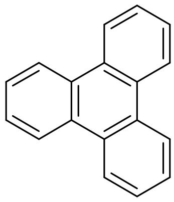
Empirical formula	$C_{44}H_{28}Br_4N_8O_{12}Pb_4Pd$
Fw	2115.54
Cryst syst	*Triclinic*
a (Å)	7.634(5)
b (Å)	13.084(8)
c (Å)	14.166(10)
α (°)	105.216(13)
β (°)	105.376(9)
γ (°)	94.884(9)
V (Å^3)	1298.2(15)
Space Group	*P-1*
Z value	1
ρcalc. (g/cm^3)	2.706
Absorption coefficient (mm^{-1})	16.409
Temp (K)	298 (2)
Data / restraints / parameters	4563 / 30 / 319
final *R* indices [I > 2sigma(I)]	*R1* = 0.0718, *wR2* = 0.1639

Table S3. Selected bond lengths [Å] and angles [°] for **B**

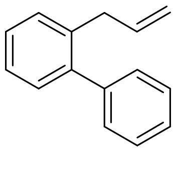
O(1)-Pb(1)#3	2.630(12)	O(1)-Pb(1)#4	2.653(13)
O(2)-Pb(1)#4	2.622(14)	O(3)-Pb(1)	2.516(13)
O(3)-Pb(2)	2.565(12)	O(4)-Pb(1)	2.639(14)
O(5)-Pb(2)	2.566(14)	O(5)-Pb(1)	2.742(13)
O(6)-Pb(2)#2	2.528(13)	Br(1)-Pb(2)	3.076(3)
Br(1)-Pb(1)#1	3.220(3)	Br(2)-Pb(2)	2.745(3)
Pd(1)-C(10)#7	2.022(17)	Pd(1)-C(12)#7	2.025(18)
Pb(2)-Br(1)-Pb(1)#1	83.17(7)	O(3)-Pb(1)-O(2)#4	82.3(5)
O(3)-Pb(1)-O(1)#5	128.4(4)	O(2)#4-Pb(1)-O(1)#5	125.4(4)
O(3)-Pb(1)-O(4)	49.2(4)	O(2)#4-Pb(1)-O(4)	126.6(5)
O(1)#5-Pb(1)-O(4)	82.6(4)	O(3)-Pb(1)-O(1)#4	125.0(4)
O(2)#4-Pb(1)-O(1)#4	47.9(4)	O(1)#5-Pb(1)-O(1)#4	80.1(4)
O(4)-Pb(1)-O(1)#4	142.6(4)	O(3)-Pb(1)-O(5)	70.5(4)
O(2)#4-Pb(1)-O(5)	67.7(5)	O(1)#5-Pb(1)-O(5)	81.1(4)
O(4)-Pb(1)-O(5)	74.9(4)	O(1)#4-Pb(1)-O(5)	69.8(4)
O(3)-Pb(1)-Br(1)#6	82.4(3)	O(2)#4-Pb(1)-Br(1)#6	71.1(3)
O(1)#5-Pb(1)-Br(1)#6	143.5(3)	O(4)-Pb(1)-Br(1)#6	114.9(3)
O(1)#4-Pb(1)-Br(1)#6	98.4(3)	O(5)-Pb(1)-Br(1)#6	132.9(3)
O(6)#2-Pb(2)-O(3)	136.0(4)	O(6)#2-Pb(2)-O(5)	64.2(4)
O(3)-Pb(2)-O(5)	72.7(4)	O(6)#2-Pb(2)-Br(2)	85.3(4)
O(3)-Pb(2)-Br(2)	88.6(3)	O(5)-Pb(2)-Br(2)	92.6(3)
O(6)#2-Pb(2)-Br(1)	76.7(3)	O(3)-Pb(2)-Br(1)	146.0(3)
O(5)-Pb(2)-Br(1)	140.9(3)	Br(2)-Pb(2)-Br(1)	85.18(8)
C(10)#7-Pd(1)-C(10)	180.000(4)	C(10)#7-Pd(1)-C(12)	97.2(7)
C(10)-Pd(1)-C(12)	82.8(7)	C(12)-Pd(1)-C(12)#7	180.0(9)

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z #2 -x+1,-y+1,-z+2 #3 x+1,y+1,z
#4 -x+1,-y+2,-z+2 #5 x-1,y-1,z #6 x-1,y,z #7 -x,-y+2,-z+1

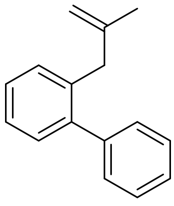
Characterization data for 4 and 5a-5j.



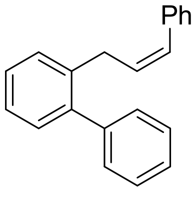
4, white solid, mp:197-198°C; ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.68 (dd, *J* = 3.0 6.0 Hz, 6H), 8.68 (dd, *J* = 3.0 6.0 Hz, 6H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 123.3, 127.2, 129.8; IR (KBr): 3097, 3074, 1988, 981, 856, 766 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{13}^+$ ($[M+H]^+$) 229.1012, found 229.0973. Anal. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 95.15; H, 5.24.



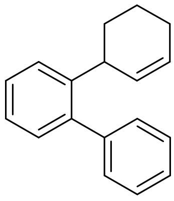
5a, yellow liquid. ^{1}H NMR (300 Hz, $CDCl_3$) δ 3.35 (d, *J* = 6.0 Hz, 2H), 4.90-5.04 (q, 2H), 5.80 (m, 1H), 7.27-7.60 (m, 9H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 36.2, 112.6, 126.6, 126.9, 127.5, 128.1 (2C), 129.0 (2C), 129.7, 130.6, 142.3, 142.5, 145.2, 146.1; IR (KBr): 3059, 3021, 1636, 1496, 1479, 745, 723 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{15}^+$ ($[M+H]^+$) 195.1168, found 195.1153. Anal. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 93.21; H, 7.41.



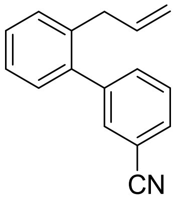
5b, yellow liquid. ^{1}H NMR (300 Hz, $CDCl_3$) δ 1.61 (s, 3H), 3.26 (s, 2H), 4.49 (s, 1H), 4.79 (s, 1H), 7.26-7.37 (m, 9H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 22.6, 41.3, 112.1, 126.1, 126.8, 127.2, 127.9 (2C), 129.2 (2C), 130.0, 130.1, 136.8, 141.8, 142.3, 145.6; IR (KBr): 3060, 3022, 2926, 1730, 1499, 890, 772, 722, 701 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{17}^+$ ($[M+H]^+$) 209.1325, found 209.1316. Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.46; H, 7.96.



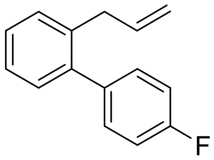
5c, yellow liquid. ^{1}H NMR (300 Hz, $CDCl_3$) δ 3.48 (s, 2H), 6.23 (s, 2H), 7.16-7.37 (m, 14H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 36.8, 126.1 (2C), 126.3, 127.0, 127.1, 127.4, 128.1 (2C), 128.6 (2C), 128.8, 129.4 (2C), 129.7, 129.8, 130.2, 131.0, 137.5, 137.7, 141.7, 142.1; IR (KBr): 3446, 3058, 3024, 2924, 1693. 1597, 1479, 1449, 1073, 1009, 746, 700 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{19}^+$ ($[M+H]^+$) 271.1481, found 271.1460. Anal. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.40; H, 6.84.



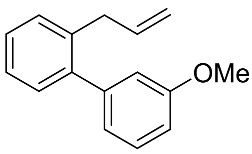
5d, yellow liquid. ^{1}H NMR (300 Hz, CDCl$_3$) δ 1.46-1.54 (d, 2H), 1.70 (s, 1H), 1.84 (s, 1H), 1.97-2.06 (m, 2H), 3.55 (s, 1H), 5.61 (s, 1H), 5.82 (s, 1H), 7.20-7.38 (m, 9H); ^{13}C NMR (75 Hz, CDCl$_3$) δ 21.7, 24.9, 32.4, 37.9, 125.6, 126.8, 127.5, 127.8, 127.9, 128.0 (2C), 129.4 (2C), 130.0, 131.1, 141.7, 141.9, 144.1; IR (KBr): 3057, 3019, 2931, 2856, 1477, 1445, 755, 720 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{19}^{+}$ ([M+H]$^{+}$) 235.1481, found 235.1465. Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.57; H, 7.65.



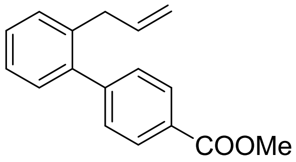
5e, yellow liquid. ^{1}H NMR (300 Hz, CDCl$_3$) δ 3.28 (s, 2H), 4.87 (d, *J* = 12.6 Hz, 1H), 5.02 (d, *J* = 0.9 Hz, 1H), 5.85 (m, 1H), 7.18 (s, 1H), 7.30-7.35 (m, 3H), 7.51-7.55 (m, 2H), 7.62 (s, 2H); ^{13}C NMR (75 Hz, CDCl$_3$) δ 37.4, 112.3, 116.2, 118.8, 126.5, 128.4, 128.9, 129.9, 130.2, 130.6, 132.7, 133.7, 137.0, 137.2, 139.6, 143.9; IR (KBr): 3399, 3061, 2924, 2853, 2229, 1636, 1492, 760, 698 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{14}N^{+}$ ([M+H]$^{+}$) 220.1121, found 220.1118. Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.28; H, 5.66; N, 6.42.



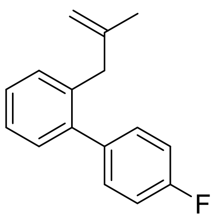
5f, yellow liquid. ^{1}H NMR (300 Hz, CDCl$_3$) δ 3.30 (s, 2H), 4.86 (d, *J* = 12.9 Hz, 1H), 5.01 (d, *J* = 6.6 Hz, 1H), 5.86 (t, 1H), 7.06 (s, 2H), 7.20-7.40 (m, 6H); ^{13}C NMR (75 Hz, CDCl$_3$) δ 38.3, 115.7 (d, *J* = 22.5 Hz, 1C), 116.7, 127.0, 128.4, 130.7, 131.0, 131.6, 131.7, 132.1, 137.1, 138.0, 138.5, 161.3, 164.5; IR (KBr): 3062, 2957, 2925, 1637, 1513, 1445, 1220, 1142, 839, 761 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{14}F^{+}$ ([M+H]$^{+}$) 213.1074, found 213.1090. Anal. Calcd for $C_{15}H_{13}F$: C, 84.88; H, 6.17. Found: C, 84.80; H, 6.24.



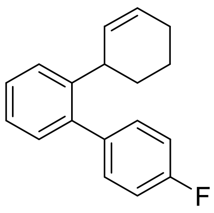
5g, yellow liquid. ^{1}H NMR (300 Hz, CDCl$_3$) δ 3.34 (s, 2H), 3.79 (s, 3H), 4.92 (d, *J* = 12.6 Hz, 1H), 5.01 (d, *J* = 6.9 Hz, 1H), 5.90 (m, 1H), 6.87 (d, *J* = 5.7 Hz, 3H), 7.26 (d, *J* = 12.9 Hz, 5H); ^{13}C NMR (75 Hz, CDCl$_3$) δ 37.5, 55.2, 112.6, 114.9, 115.8, 121.8, 126.1, 127.5, 129.0, 129.8, 130.0, 137.2, 137.9, 141.7, 143.1, 159.8; IR (KBr): 3059, 3002, 2937, 2834, 1688, 1597, 1475, 1221, 1044, 758, 703 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{17}O^{+}$ ([M+H]$^{+}$) 225.1274, found 225.1260. Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.82; H, 7.33.



5h, yellow liquid. ^{1}H NMR (300 Hz, CDCl$_3$) δ 3.35 (d, *J* = 6.0 Hz, 2H), 3.97 (s, 3H), 4.92 (d, *J* = 18 Hz, 1H), 5.04 (d, *J* = 12 Hz, 1H), 5.83-6.03 (m, 1H), 7.24-7.47 (m, 6H), 8.05 (d, *J* = 18 Hz, 2H); ^{13}C NMR (75 Hz, CDCl$_3$) δ 37.4, 52.1, 116.0, 126.3, 128.0, 128.8, 129.3 (2C), 129.4 (2C), 129.8, 130.0, 137.0, 137.5, 141.0, 146.5, 167.0; IR (KBr): 3421, 3060, 2950, 2843, 1724, 1610, 1278, 1113, 779, 754 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{17}O_{2}^{+}$ ([M+H]$^{+}$) 253.1223, found 253.1202. Anal. Calcd for $C_{17}H_{16}O_{2}$: C, 80.93; H, 6.39. Found: C, 81.08; H, 6.53.

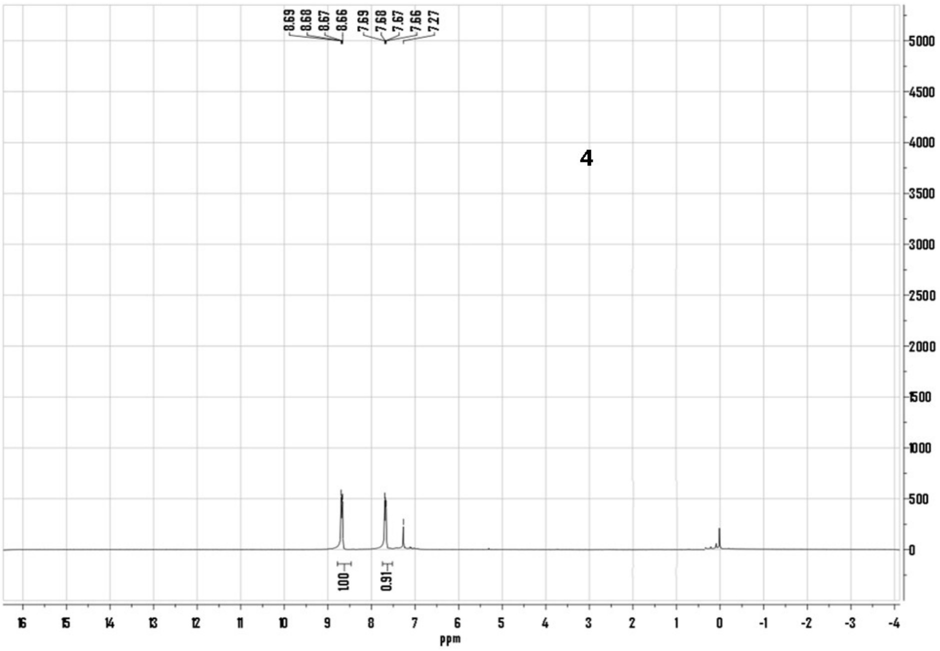


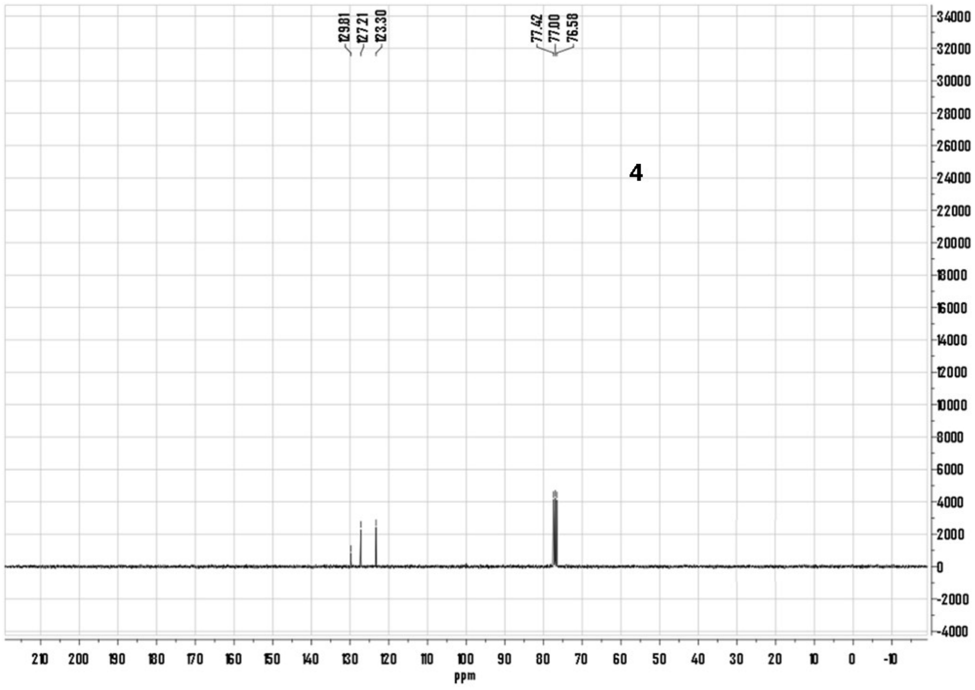
5i, yellow liquid. ^{1}H NMR (300 Hz, $CDCl_3$) δ 1.61 (s, 3H), 3.22 (s, 2H), 4.45 (s, 1H), 4.79 (s, 1H), 7.06 (s, 2H), 7.26 (d, *J* = 1.2 Hz, 6H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 23.5, 42.15, 113.0, 115.6 (d, *J* = 22.5 Hz, 1C), 127.0, 128.2, 130.9, 131.1, 131.5, 137.8, 138.4, 138.5, 142.1, 146.3, 161.2, 164.5; IR (KBr): 3446, 3067, 2926, 1650, 1512, 1481, 1222, 1157, 838, 762 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{16}F^{+}$ ($[M+H]^{+}$) 227.1231, found 227.1235. Anal. Calcd for $C_{16}H_{15}F$: C, 84.92; H, 6.68. Found: C, 85.02; H, 6.74.



5j, yellow liquid. ^{1}H NMR (300 Hz, $CDCl_3$) δ 1.48-1.60 (m, 2H), 1.75-1.80 (m, 1H), 1.84-1.91 (m, 1H), 2.02-2.11 (m, 2H), 3.55 (s, 1H), 5.66 (d, *J* = 9.9 Hz, 1H), 5.99 (d, *J* = 10.5 Hz, 1H), 7.04-7.40 (m, 8H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 22.5, 25.7, 33.2, 38.7, 115.8 (d, *J* = 15.0 Hz, 1C), 126.5, 128.3, 128.5 (2C), 128.9, 130.8, 131.7, 137.1, 138.6, 141.4, 145.1, 161.2, 164.4; IR (KBr): 3061, 3020, 2931, 2856, 1437, 1445, 852, 760 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{18}F^{+}$ ($[M+H]^{+}$) 253.1387, found 253.1379. Anal. Calcd for $C_{18}H_{17}F$: C, 85.68; H, 6.79. Found: C, 85.83; H, 6.87.

^{1}H NMR and ^{13}C NMR spectra.

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127.21
123.30
77.42
77.00
76.58
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
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4000
2000
0
-2000
-4000
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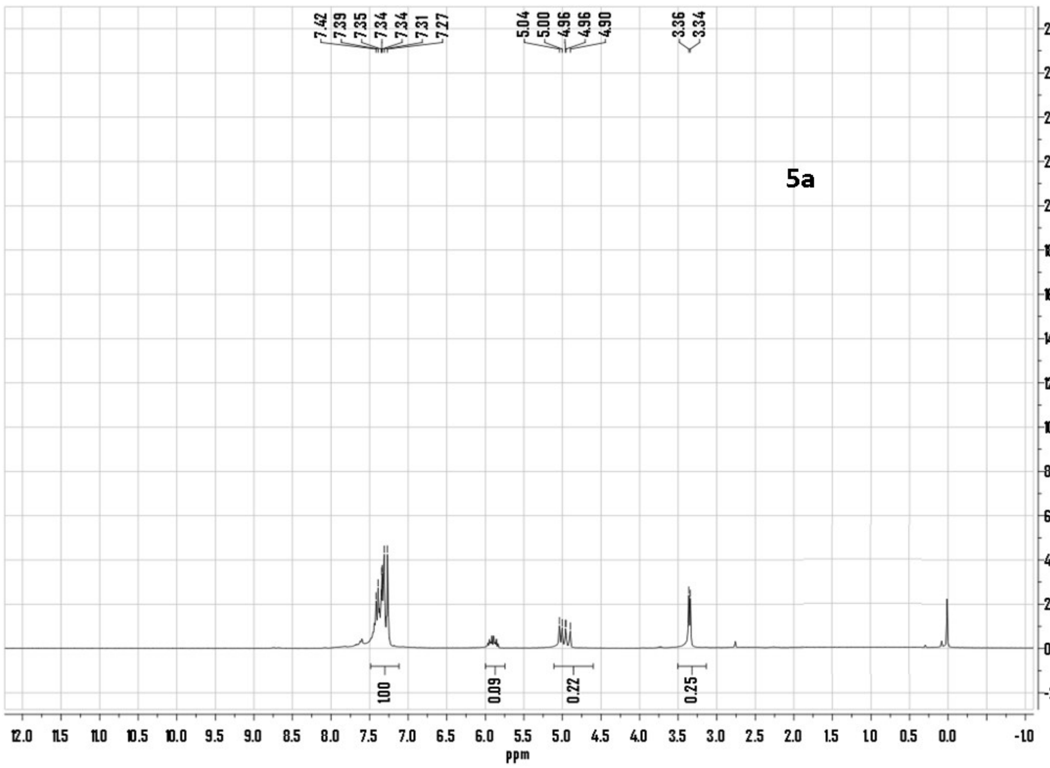
ppm

4


7.42
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7.35
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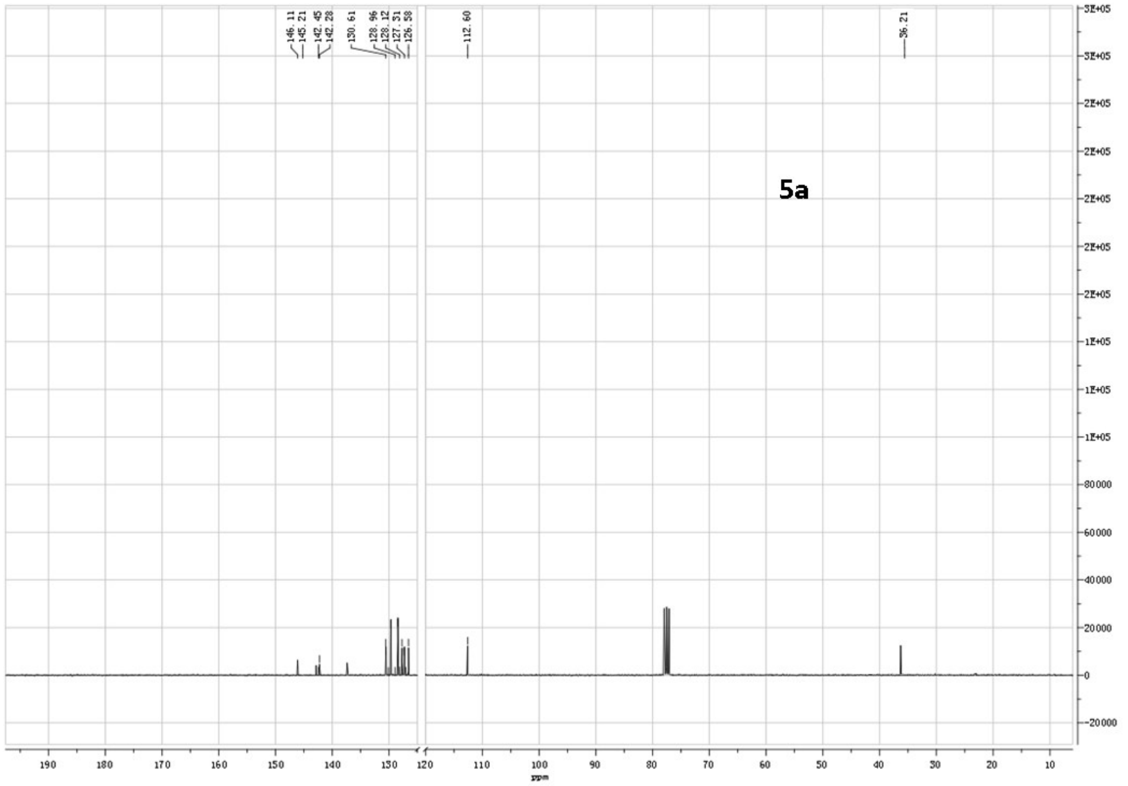
7.34
7.31
7.27
5.04
5.00
4.96
4.96
4.90
3.36
3.34
1.00
0.09
0.22
0.25
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
ppm

5a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145.21
142.45
142.28
130.61
128.96
128.12
127.31
126.58
112.60
36.21
5a
3E+05
3E+05
2E+05
2E+05
2E+05
2E+05
2E+05
1E+05
1E+05
1E+05
80000
60000
40000
20000
0
-20000
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140
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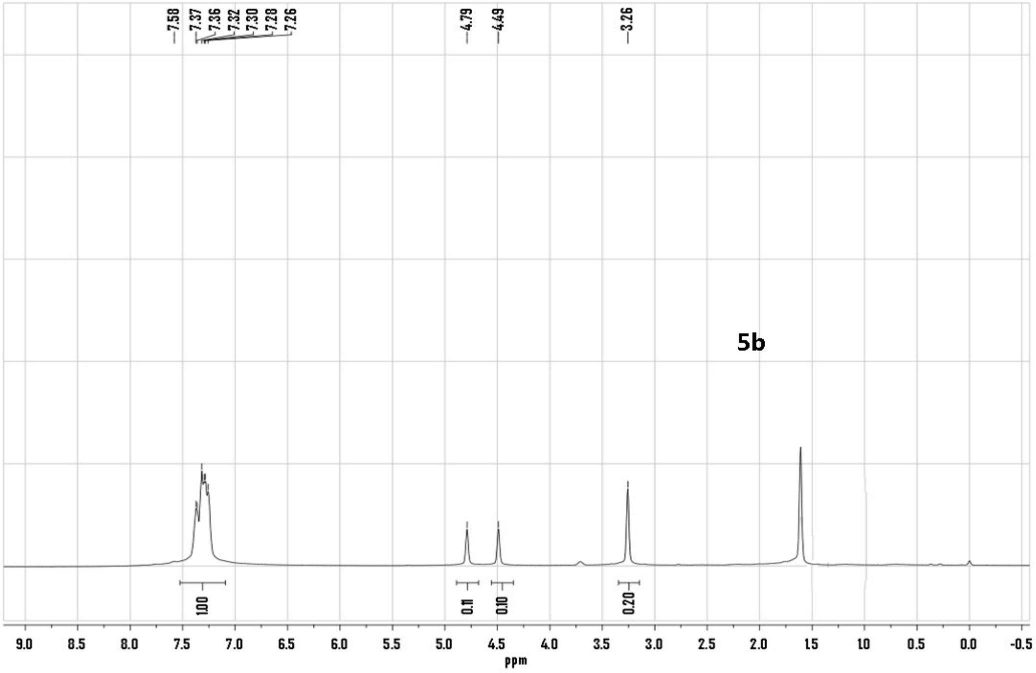
70
60
50
40
30
20
10
ppm


7.58
7.37
7.36
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7.28
7.26
4.79
4.49
3.26
5b
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0.11
0.10
0.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
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1.0
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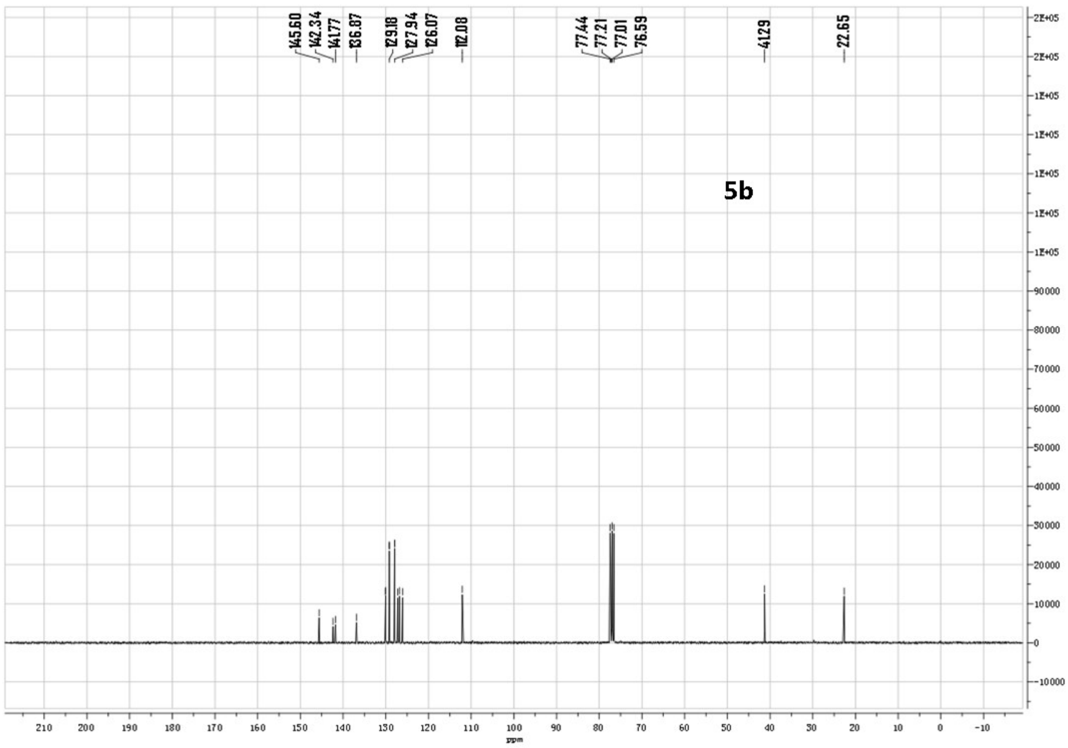
-0.5
ppm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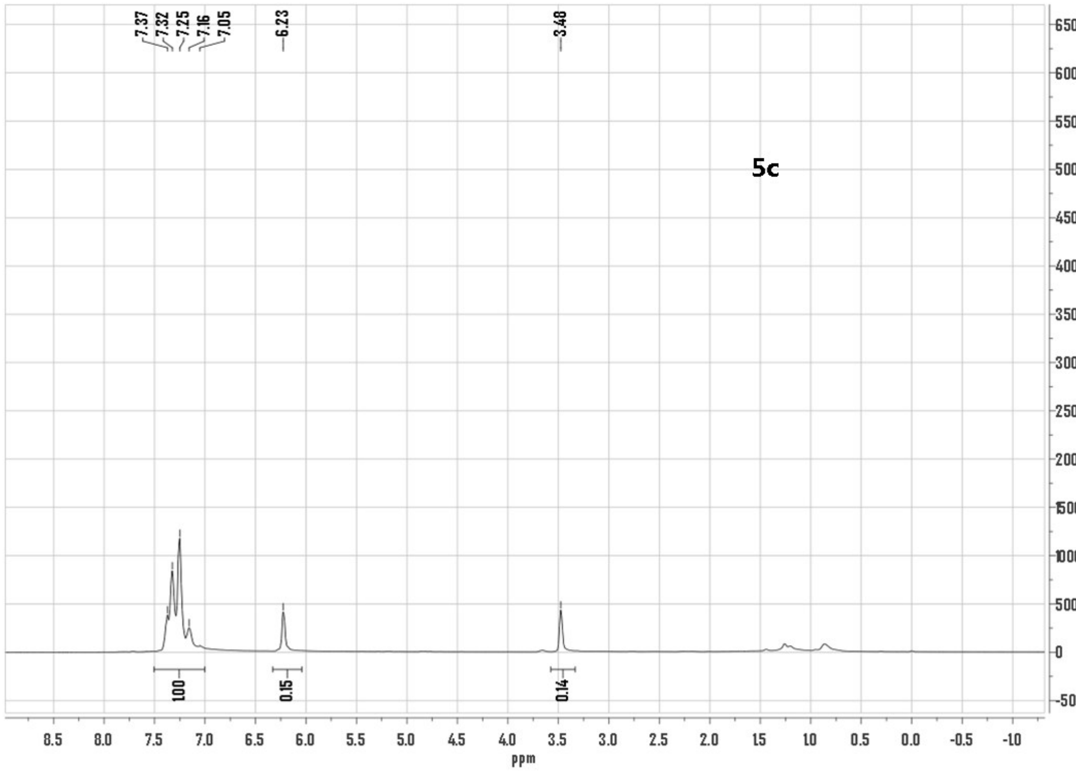
22.65
5b
ppm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6.23
3.48
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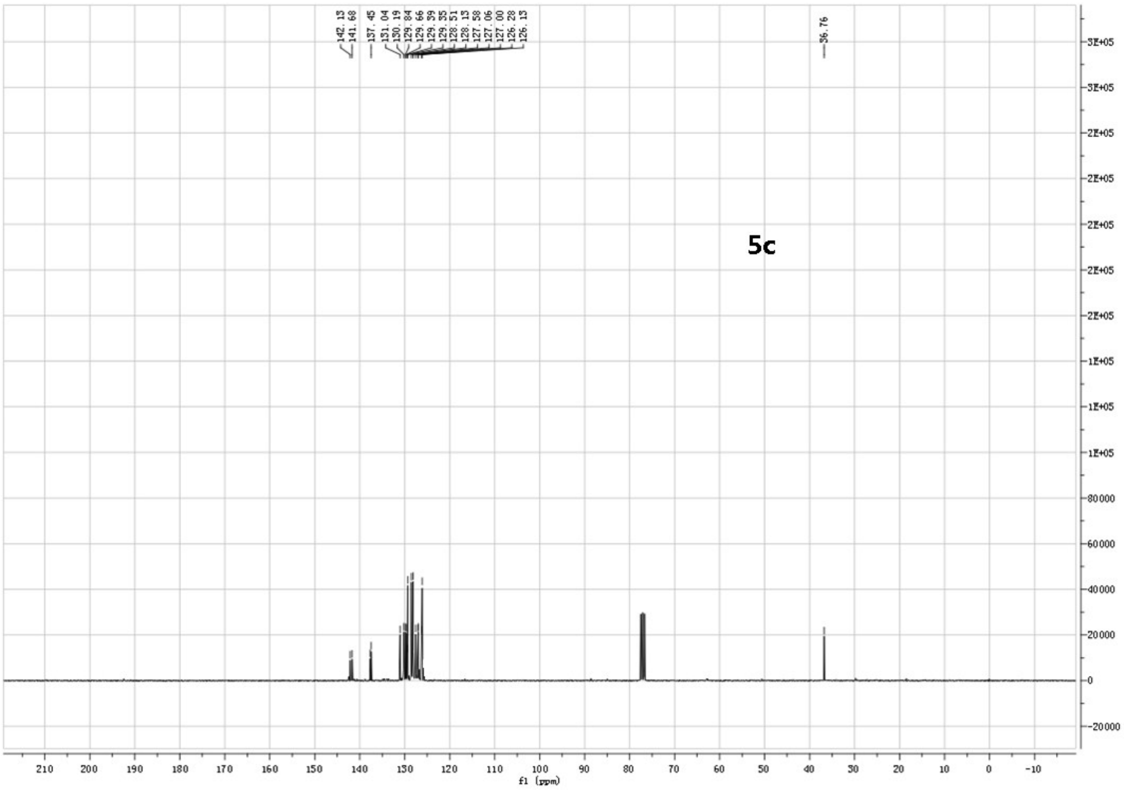
0.14
ppm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129.35
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127.58
127.06
127.00
126.28
126.13
36.76
3E+05
3E+05
2E+05
2E+05
2E+05
2E+05
2E+05
1E+05
1E+05
1E+05
80000
60000
40000
20000
0
-20000
210
200
190
180
170
160
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100
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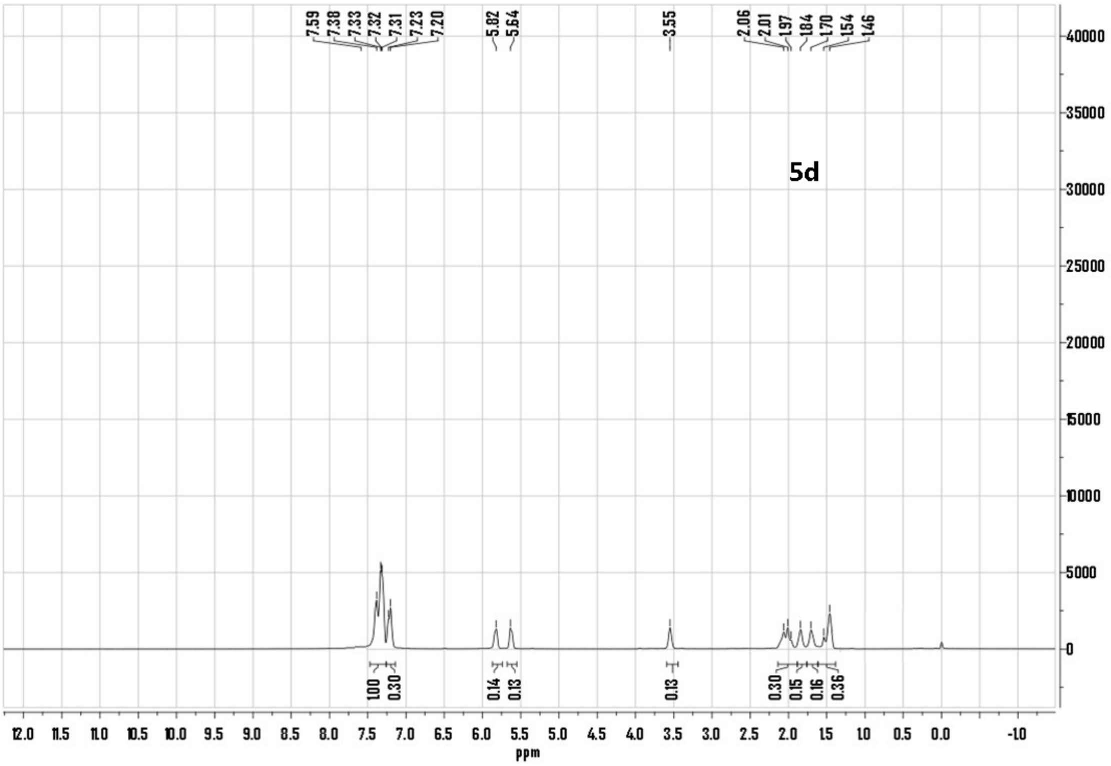
60
50
40
30
20
10
0
-10
f1 (ppm)


5d
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7.38
7.33
7.32
7.31
7.23
7.20
5.82
5.64
3.55
2.06
2.01
1.97
1.84
1.70
1.54
1.46
1.00
0.30
0.14
0.13
0.13
0.30
0.15
0.16
0.36
40000
35000
30000
25000
20000
15000
10000
5000
0
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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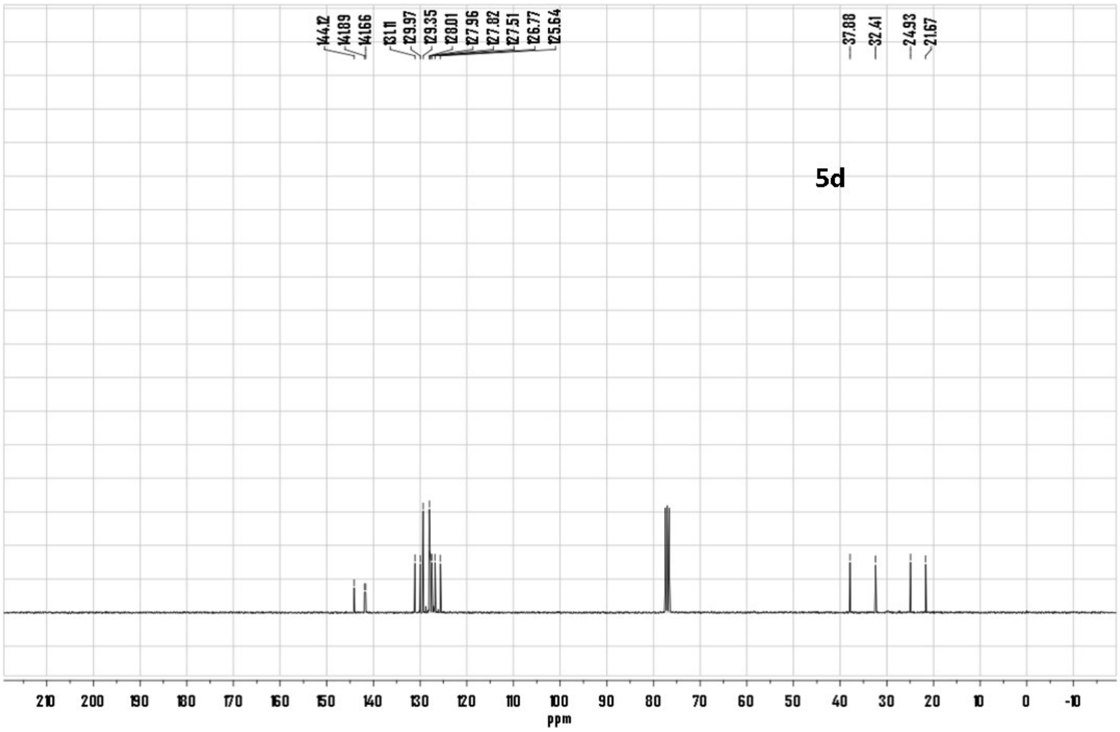
0.0
-1.0
ppm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141.66
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128.01
127.96
127.82
127.51
126.77
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37.88
32.41
24.93
21.67
5d
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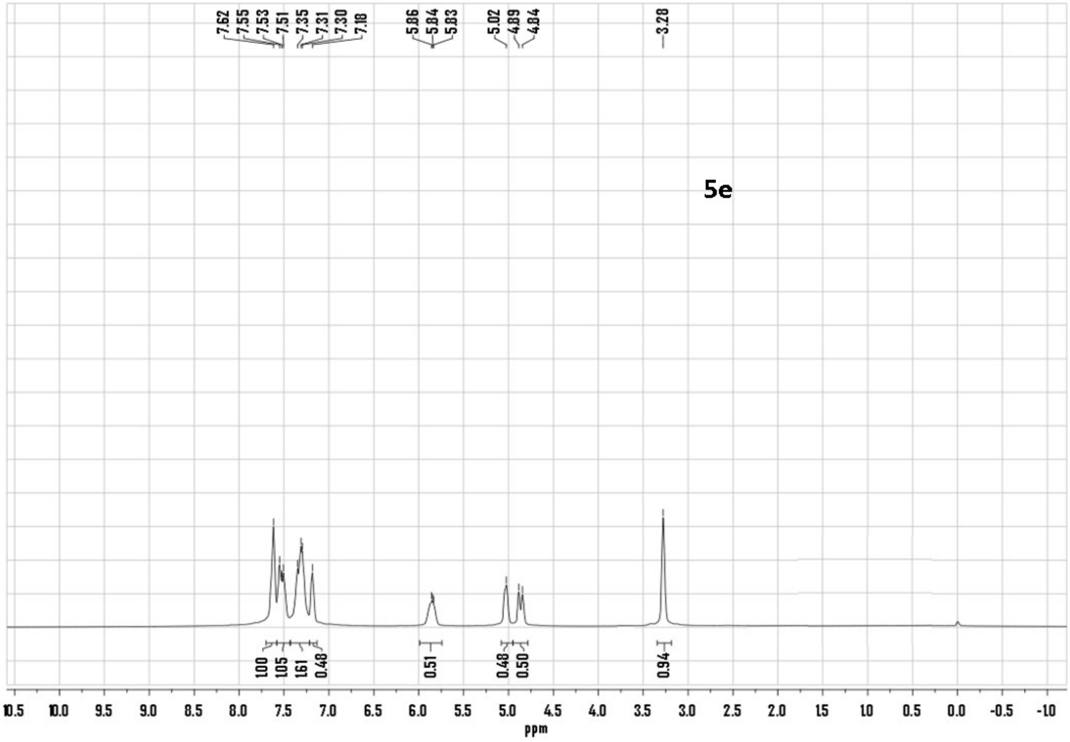
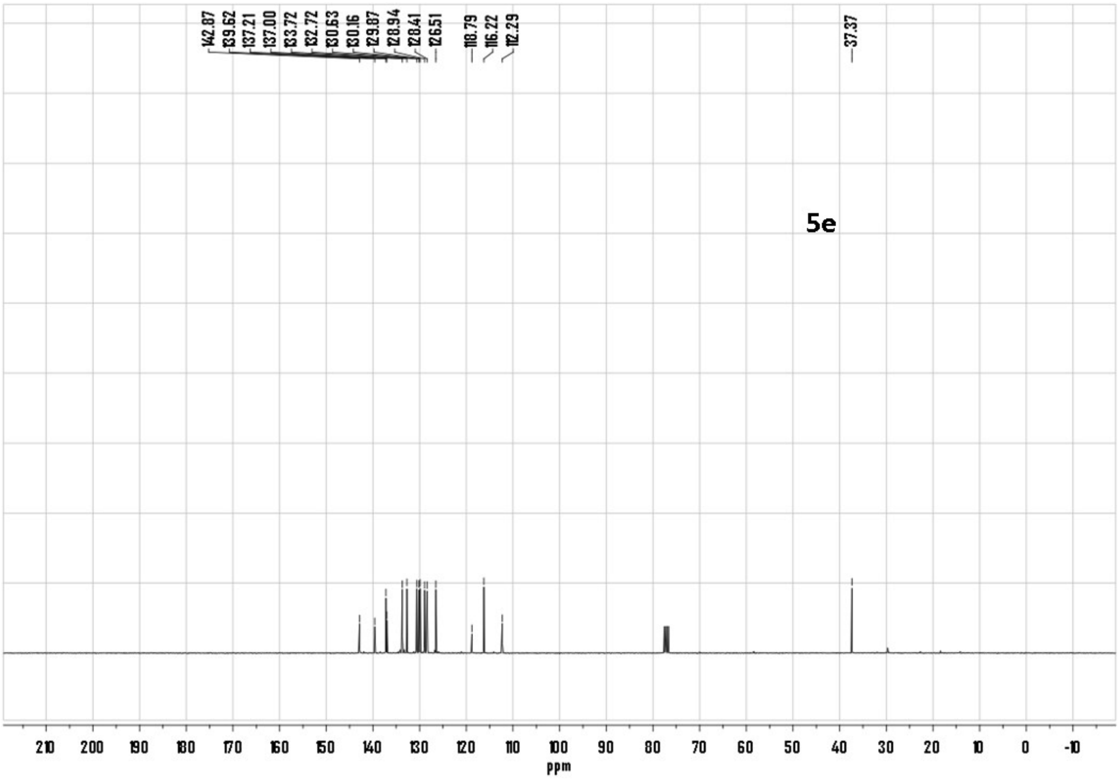
ppm


7.62
7.55
7.53
7.51
7.35
7.31
7.30
7.18
5.86
5.84
5.83
5.02
4.89
4.84
3.28
5e
1.00
1.05
1.61
0.48
0.51
0.48
0.50
0.94
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


5e
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137.21
137.00
133.72
132.72
130.63
130.16
129.87
128.94
128.41
126.51
118.79
116.22
112.29
37.37
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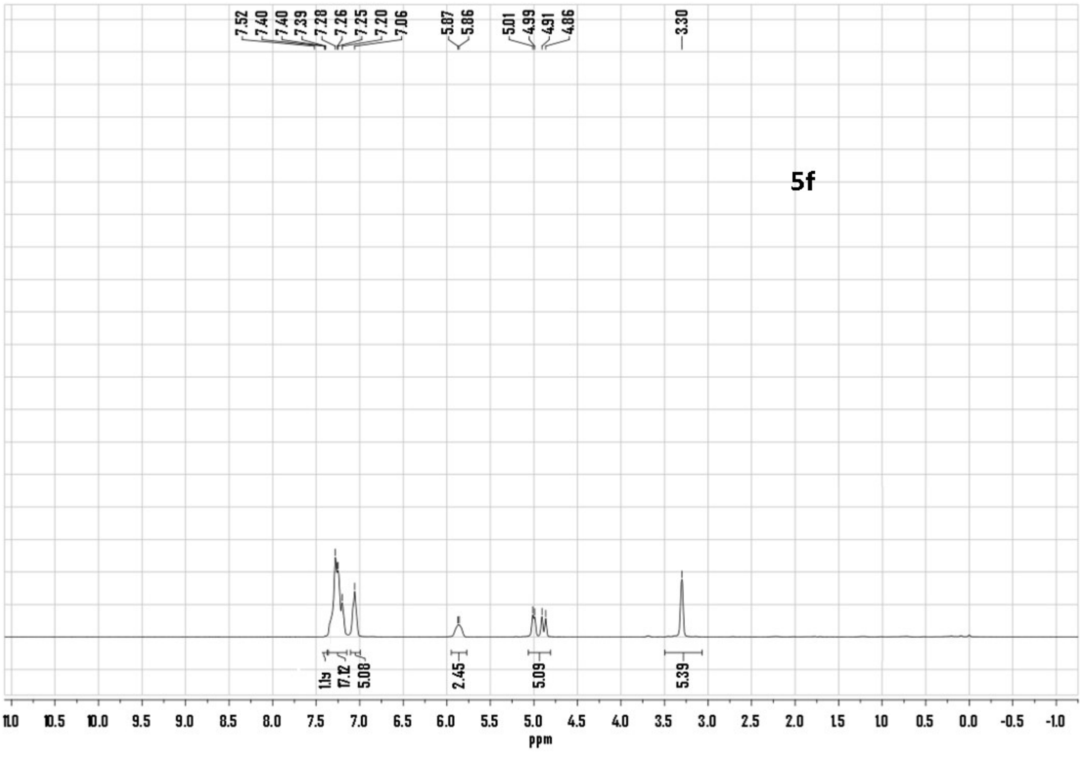
ppm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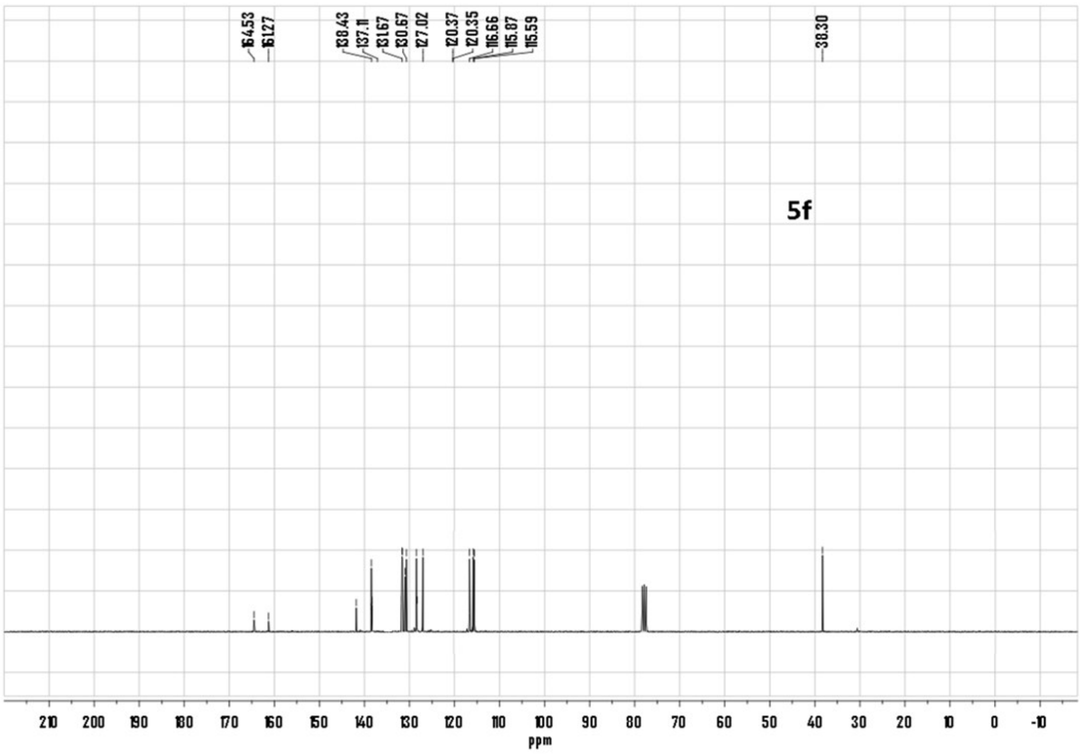
7.40
7.39
7.28
7.26
7.25
7.20
7.06
5.87
5.86
5.01
4.99
4.91
4.86
3.30
1.19
17.12
5.08
2.45
5.09
5.39
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm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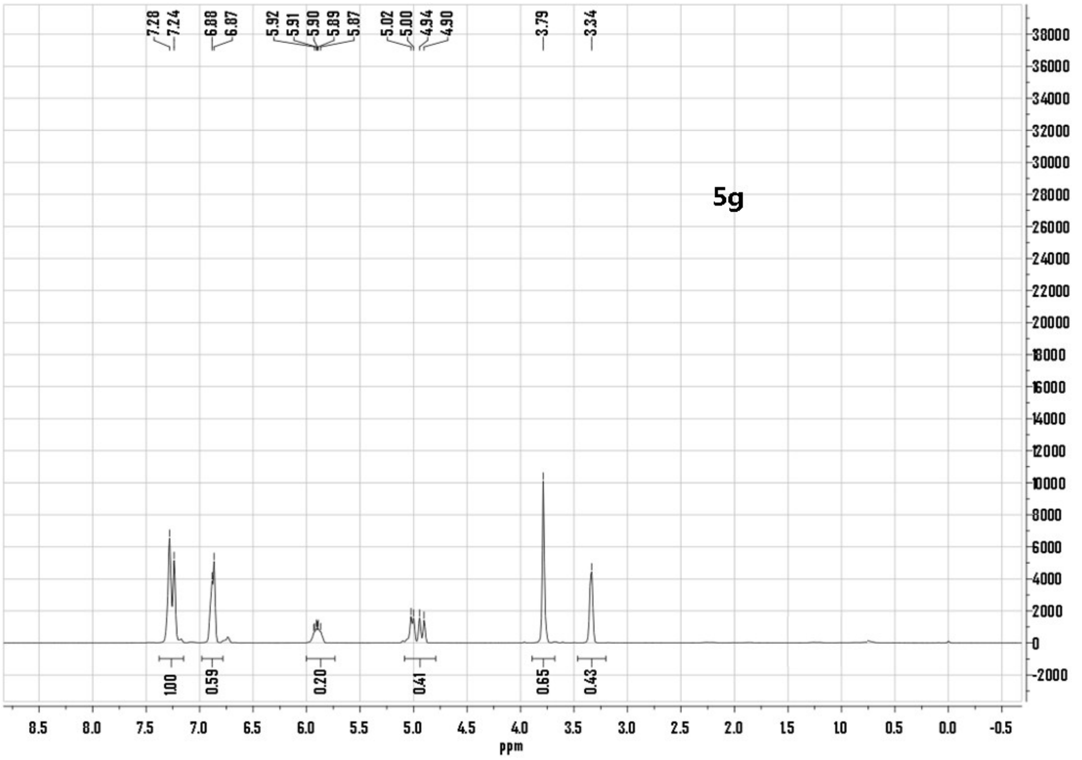
137.11
131.67
130.67
127.02
120.37
120.35
116.66
115.87
115.59
38.30
5f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm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7.24
6.88
6.87
5.92
5.91
5.90
5.89
5.87
5.02
5.00
4.94
4.90
3.79
3.34
5g
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
1.00
0.59
0.20
0.41
0.65
0.43
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
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1.0
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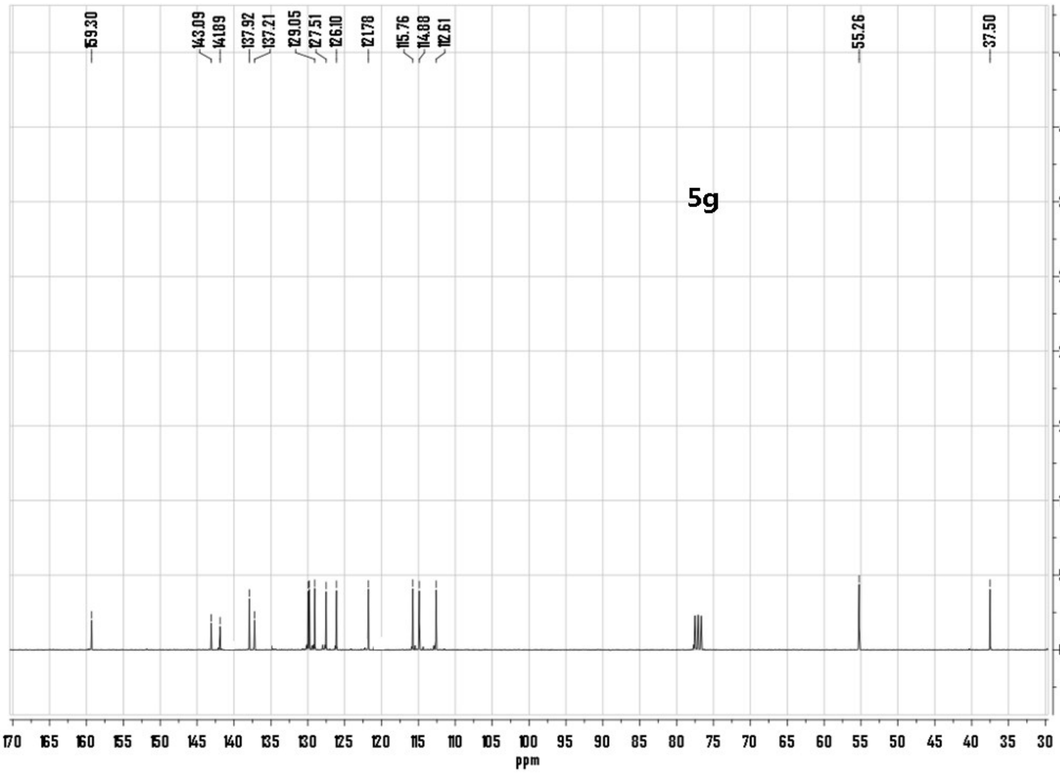
ppm


5g

159.30
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137.21
129.05
127.51
126.10
121.78
115.76
114.88
112.61
55.26
37.50
4E+05
4E+05
3E+05
2E+05
2E+05
2E+05
1E+05
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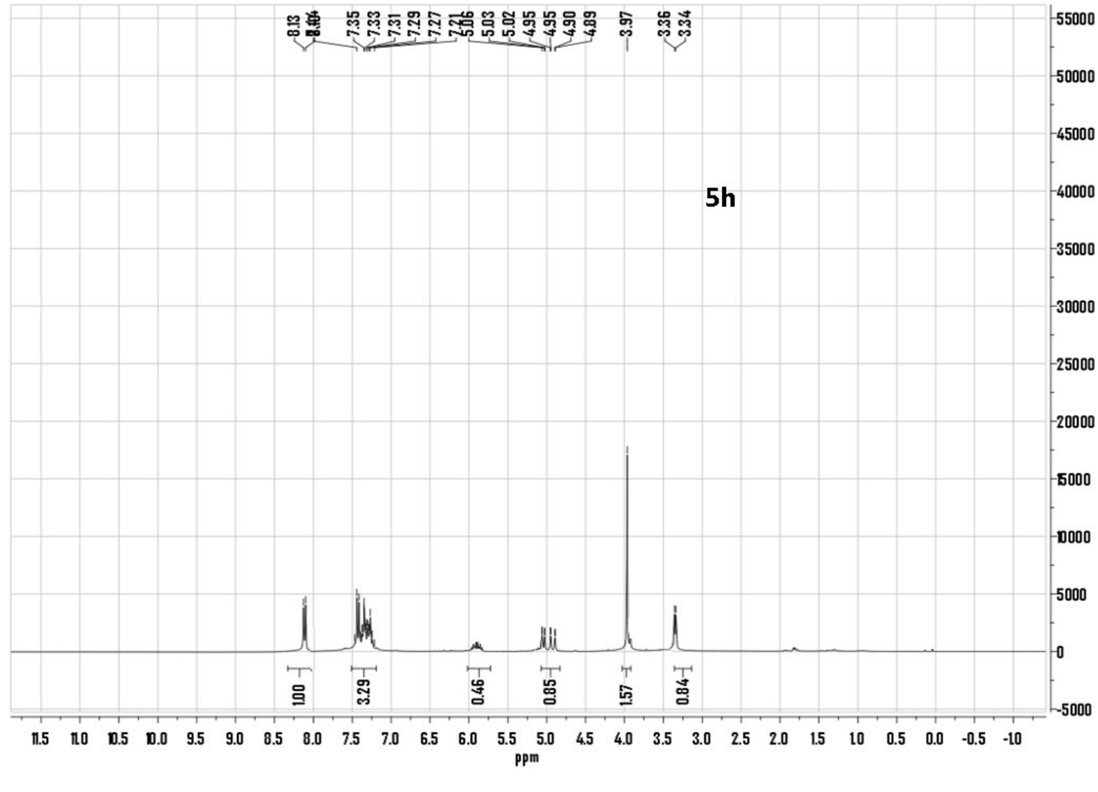
ppm


5h

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7.21
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5.03
5.02
4.95
4.95
4.90
4.89
3.97
3.36
3.34
1.00
3.29
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1.57
0.84
55000
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45000
40000
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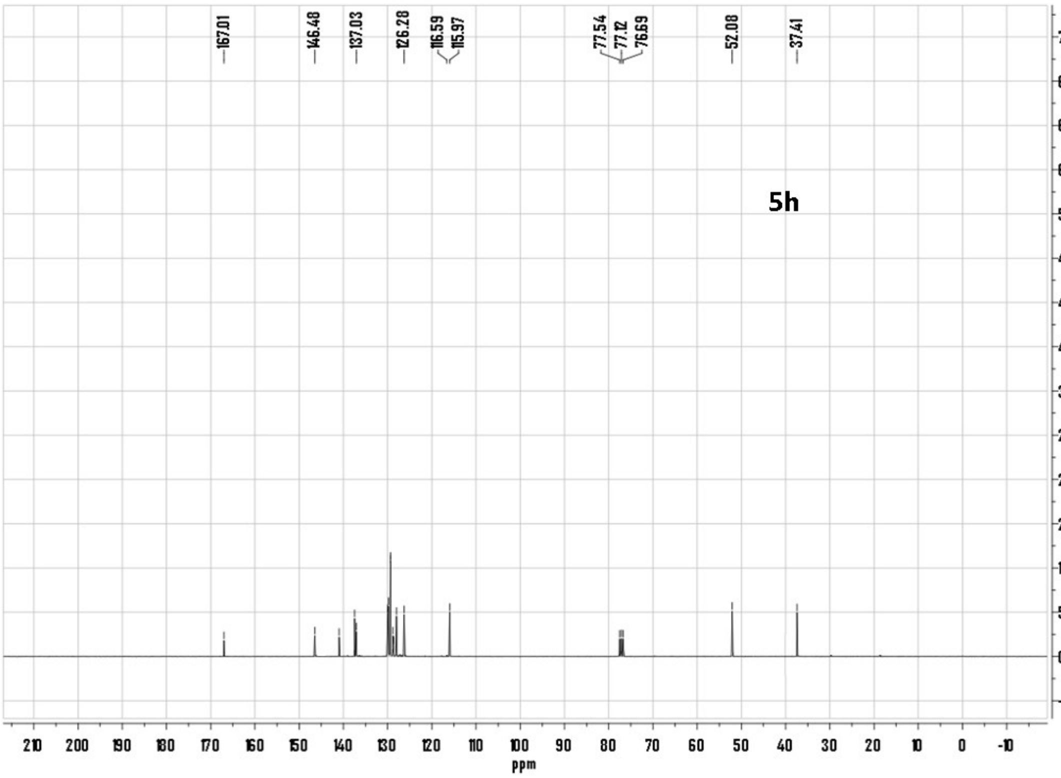
25000
20000
15000
10000
5000
0
-5000
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


5h
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7E+05
6E+05
5E+05
4E+05
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-50000
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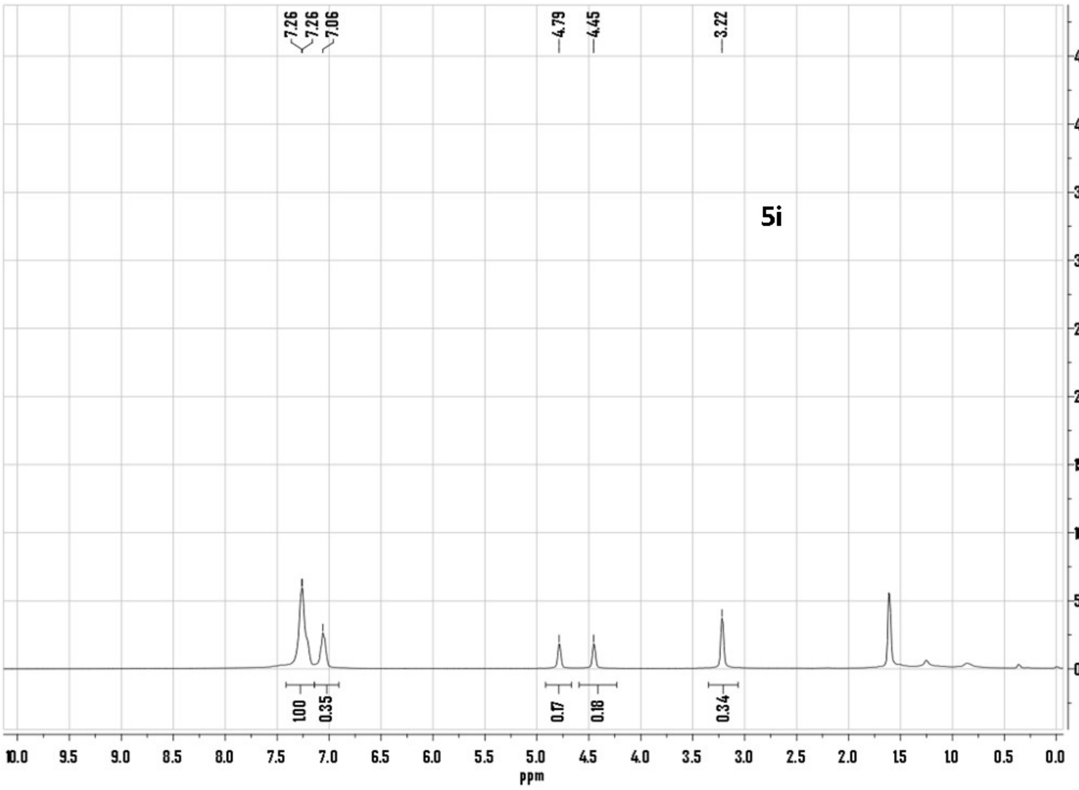
ppm


5i
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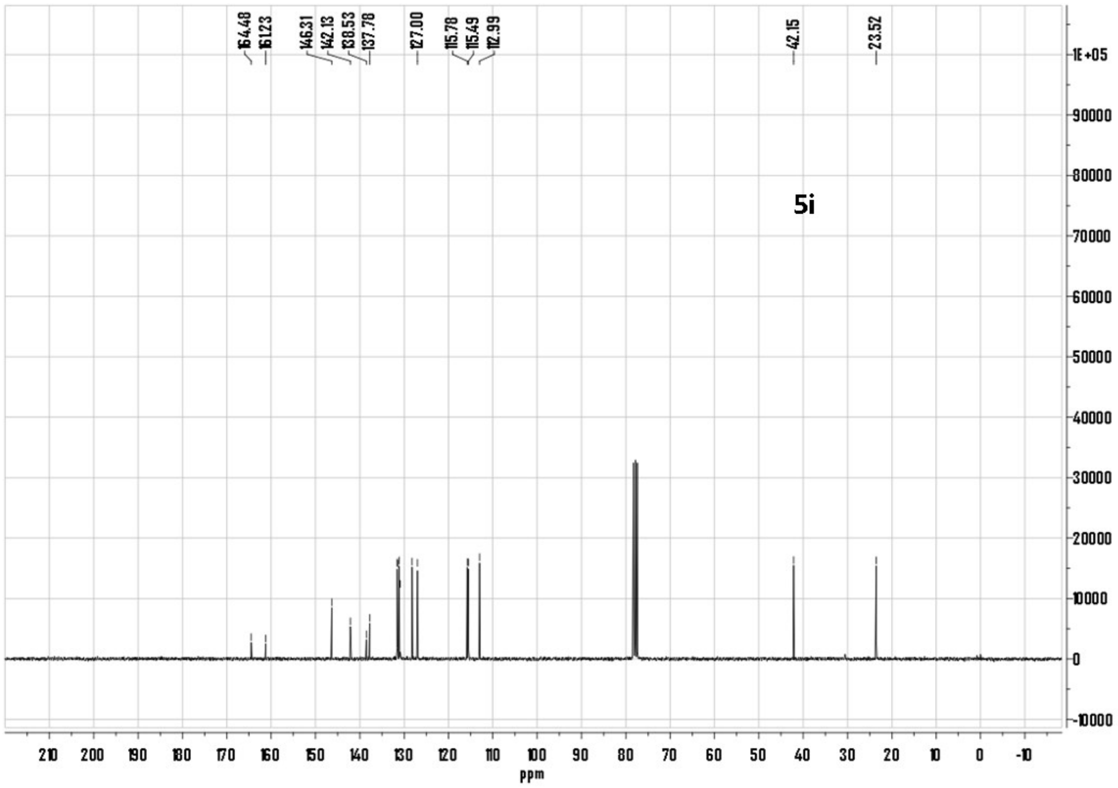
0.35
0.17
0.18
0.34
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


164.48
161.23
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112.99
42.15
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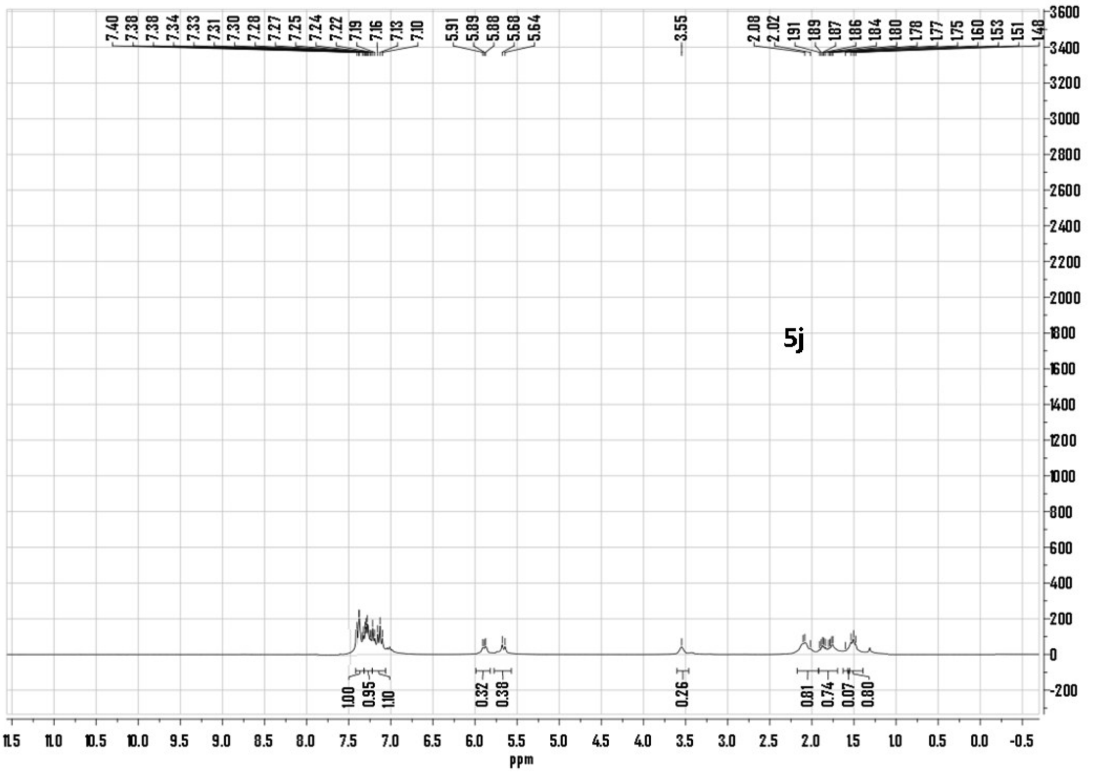
5i
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm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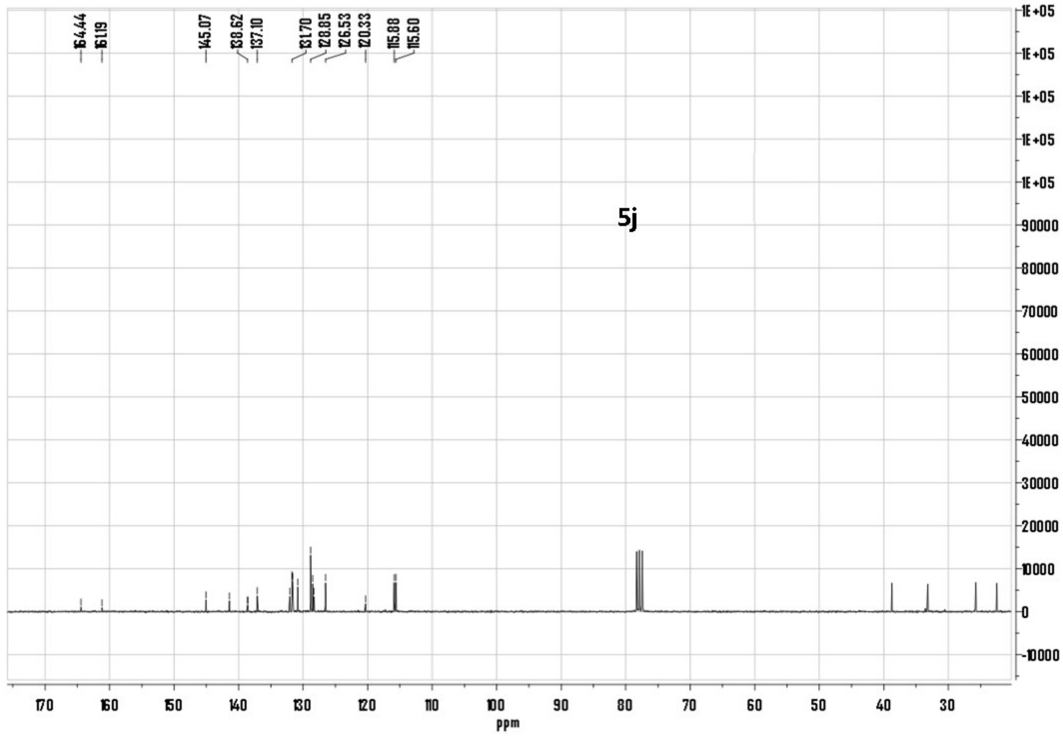
1.86
1.84
1.80
1.78
1.77
1.75
1.60
1.53
1.51
1.48
5j
1.00
0.95
1.10
0.32
0.38
0.26
0.81
0.74
0.07
0.80
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm



References

1. (a) CrysAlisPro, Agilent Technologies,Version 1.171.36.32 (release 02-08-2013 CrysAlis171.NET) (compiled Aug 2 2013,16:46:58). (b) Spek, A. L. PLATON, A Multipurpose Crystallographic Tool. University of Utrecht, Utrecht, The Netherlands, 1998.
2. (a) M. Artico, R. Silvestri, G. Stefancich, L. Avigliano, A. D. Giulio, M. Maccarrone, E. Agostinelli, B. Mondovi, L. Morpurgo, *Eur. J. Med. Chem.,* 1992**, 27**, 219-228. (b) S. Ahrens, E. Herdtweck, S. Goutal, T. Strassner, *Eur. J. Inorg. Chem.,* 2006, 1268-1274. (c) L. Li, J. Wang, C. Zhou, R. Wang, M. Hong, *Green Chem.,* 2011, **13**, 2071-2077.