Design and application of diamine-based copper(I) complexes in photoredox catalysis

Electronic Supplementary Information

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Table of Contents

General Information

Unless otherwise indicated, starting materials were obtained from commercial suppliers, and were used without further purification.

Analytical thin-layer chromatography (TLC) was performed on Merck DC precoated TLC plates with 0.25 mm Kieselgel 60 F 254. Visualization was performed with a 254 nm UV lamp.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-250 in $CDCl_3$, DMSO-d_6 and acetone-d_6. Solvents' residual proton peaks were used as standards. Chemical shifts (δ) are reported in ppm, coupling constants (*J*) are reported in Hertz (Hz). Splitting patterns are designated as s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), h (hextet), hept (heptet) and m (multiplet).

All melting points were measured on Büchi 501 apparatus and are uncorrected.

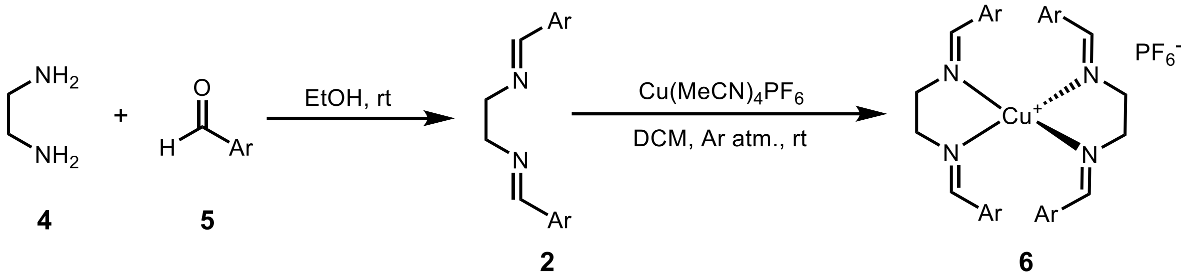
IR spectra were obtained from the solid products using ATR on a Bruker Alpha FT-IR (from 4000 cm-1to 375 cm-1) or a Mettler Toledo ReactIR 15 with AgX DiComp probe (6 mm x 1.5 m Fiber (Silver Halide)) and MCT detector (from 3000 cm-1 to 650 cm-1).

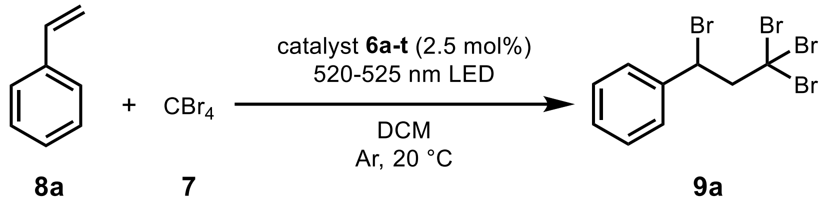
UV-VIS spectra for copper complexes were obtained on AvaSpec-ULS2048L-EVO-RS 330-850nm modular spectrometer using 10 µm slit, FDP-7UV200-2-5mm 2m fiber optics mounted with FDP-TIP-1mm tip probe (equals with 2mm cuvette, resolution ~ 0.5 nm) and processed by AvaSoft. Spectra of solutions were recorded in CH_2Cl_2 solvent with given concentrations.

High-resolution mass spectra were acquired on an Agilent 6230 time-of-flight mass spectrometer equipped with a Jet Stream electrospray ion source in positive ion mode. Injections of 0.1-0.3 µl were directed to the mass spectrometer at a flow rate 0.5 ml/min (70% acetonitrile-water mixture, 0.1 % formic acid), using an Agilent 1260 Infinity HPLC system.

The photoreactions carried out in our own designed temperature-adjusted photoreactor using 10W green LEDs. Thermostat: Julabo CD-300F. For further specifications read later the “The arrangement of our photoreactor” chapter.

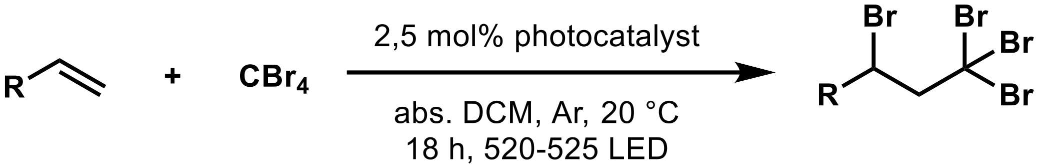
Summary of yields of Compounds 2 and 6; and full table of ligand optimization

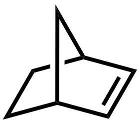
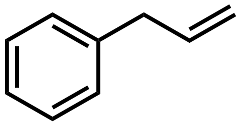




Entry	**Aldehyde**	Ar (in **5**, **2** and **6**)	Yield (**2**, %)	Yield (**6**, %)	Yield (**9a**, %)
1	**5a**	C_6H_5	85	80	73
2	**5b**	4-Me_2N- C_6H_4	82	75	8
3	**5c**	4-MeO-C_6H_4	44	86	53
4	**5d**	2-MeO-C_6H_4	82	92	76
5	**5e**	2-Ph-C_6H_4	70	94	88
6	**5f**	4-Cl-C_6H_4	90	92	62
7	**5g**	3-Cl-C_6H_4	88	53	79
8	**5h**	2-Cl-C_6H_4	82	89	90
9	**5i**	2,4-Cl_2-C_6H_3	88	95	83
10	**5j**	2,6-Cl_2-C_6H_3	88	93	4
11	**5k**	2-F-C_6H_4	51	88	88
12	**5l**	4-Br-C_6H_4	95	91	88
13	**5m**	2-Br-C_6H_4	69	74	93
14	**5n**	4-F-C_6H_4	71	78	83
15	**5o**	3-F-C_6H_4	75	96	76
16	**5p**	4-F_3C-C_6H_4	76	90	88
17	**5q**	2,4-F_2-C_6H_3	79	87	84
18	**5r**	3-Br-C_6H_4	65	91	83
19	**5s**	3-MeO-C_6H_4	53	85	55
20	**5t**	2-F-4-Br-C_6H_3	91	81	81

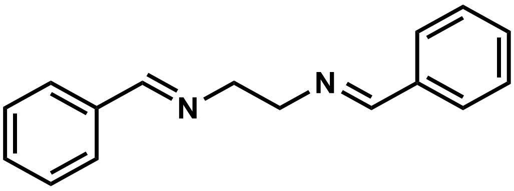
Experiments with other unsaturated compounds



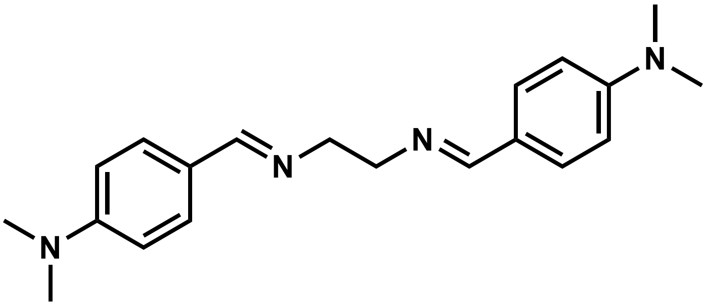
Entry	**Substrate**	**Catalyst**	**GC-MS conversion** (%)
1		**6c**	52
2		**6m**	0
3		**6c**	8
4		**6m**	0

General procedure for preparation of the diimine ligands

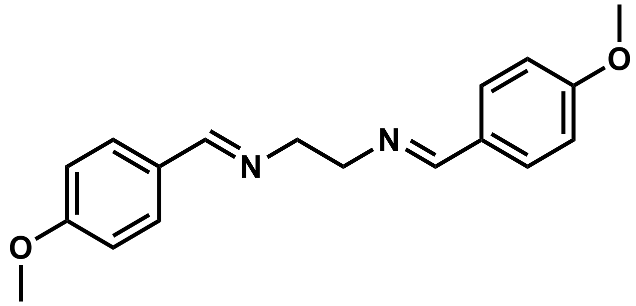
Ethylenediamine (**4**, 267 μL, 4 mmol) was dissolved in EtOH (10 mL), then the appropriate aldehyde (**5**, 8 mmol) was added. The mixture was stirred at room temperature. After 3 h, the precipitate was filtered and dried *in vacuo*. If no precipitate formed, water (10 mL) was added to the reaction mixture, then it was stirred for 20-30 min, then stored in refrigerator overnight. The precipitate was collected by filtration and was dried *in vacuo*. The products obtained were used in the next step without further purification.



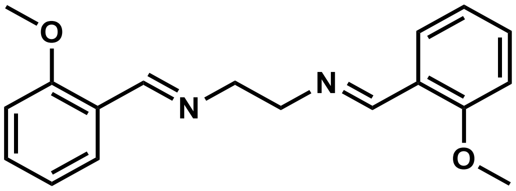
***N,N*'-(Ethane-1,2-diyl)*bis*(1-phenylmethanimine) (2a).**[1] Yield: 0.80 g (3.4 mmol, 85%), white crystals, **MP:** 54-55 °C. **IR** (ATR, cm^{-1}): 1644, 1450, 751, 692. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 8.29 (s, 2H), 7.70 (dd, *J* = 6.9, 2.9 Hz, 4H), 7.52 – 7.30 (m, 6H), 3.98 (s, 4H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 162.8, 136.2, 130.7, 128.7, 128.2, 61.8.



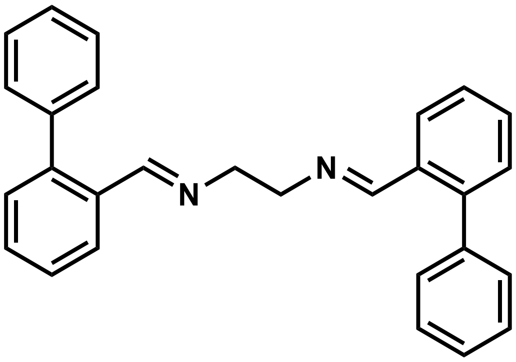
4,4'-((Ethane-1,2-diylbis(azaneylylidene))*bis*(methaneylylidene))*bis*(*N,N*-dimethylaniline) (2b).[2] Yield: 1.06 g (3.3 mmol, 82%), white crystals, **MP:** 176-177 °C. **IR** (ATR, cm^{-1}): 1640, 1601, 1529, 1443, 1363, 1342, 1309, 1225, 1173, 1040, 949, 904, 885, 837, 809. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 8.16 (s, 2H), 7.57 (d, *J* = 8.8 Hz, 4H), 6.67 (d, *J* = 8.8 Hz, 4H), 3.87 (s, 4H), 3.00 (s, 12H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 162.5, 152.1, 129.6, 124.7, 111.7, 62.2, 40.4.



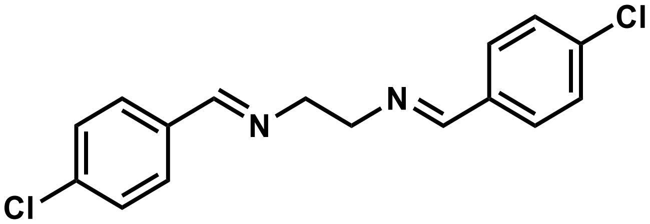
***N,N*'-(Ethane-1,2-diyl)*bis*(1-(4-methoxyphenyl)methanimine) (2c).**[3] Yield: 0.52 g (1.8 mmol, 44%), white crystals, **MP:** 111-112 °C. **IR** (ATR, cm^{-1}): 1644, 1609, 1512, 1450, 1312, 1253, 1169, 1109, 1020, 831. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 8.20 (s, 2H), 7.63 (d, *J* = 8.5 Hz, 4H), 6.89 (d, *J* = 8.5 Hz, 4H), 3.91 (s, 4H), 3.82 (s, 6H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 162.0, 161.6, 129.7, 129.2, 114.0, 61.9, 55.5.



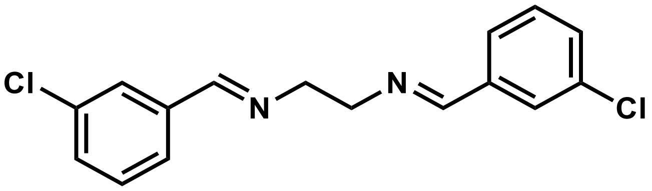
***N,N*'-(Ethane-1,2-diyl)*bis*(1-(2-methoxyphenyl)methanimine) (2d).**[3] Yield: 0.97 g (3.3 mmol, 82%), white crystals, **MP:** 114-116 °C. **IR** (ATR, cm^{-1}): 1635, 1594, 1489, 1465, 1434, 1372, 1284, 1243, 1161, 1113, 1020, 975, 770. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 8.72 (s, 2H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 6.95 (t, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 8.3 Hz, 2H), 3.97 (s, 4H), 3.78 (s, 6H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 159.3, 132.2, 127.9, 125.3, 121.2, 111.5, 62.6, 56.0.



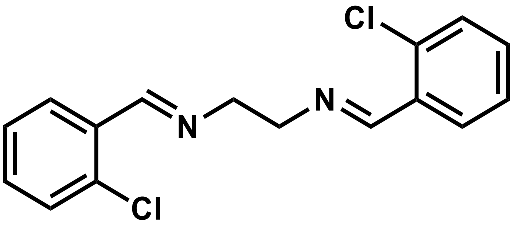
***N,N*'-(Ethane-1,2-diyl)*bis*(1-([1,1'-biphenyl]-2-yl)methanimine) (2e).** Yield: 1.10 g (2.8 mmol, 70%), wite crystals, **MP:** 115-116 °C. **IR** (ATR, cm^{-1}): 1640, 1476, 1437, 1374, 1266, 1010, 759, 748, 705. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.63 (d, *J* = 6.6 Hz, 2H), 6.86 (td, *J* = 28.4, 27.3, 5.8 Hz, 16H), 3.39 (s, 4H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 162.0, 143.1, 139.4, 133.6, 130.3, 130.2, 129.9, 128.2, 127.6, 127.4, 127.0, 61.7. **HRMS** (ESI, *m/z*) calcd for $C_{28}H_{25}N_2$ (M+H$^+$): 389.2018, found: 389.2027.



***N,N'*-(ethane-1,2-diyl)*bis*(1-(4-chlorophenyl)methanimine) (2f).**[4] Yield: 1.57 g (3.6 mmol, 90%). white crystals, **MP:** 144-145 °C. **IR** (ATR, cm^{-1}): 1646, 1596, 1571, 14876, 1374, 1281, 1083, 1014, 982, 971, 861, 837, 815, 703. **^{1}H NMR** (250 MHz, CDCl$_3$) δ 8.22 (s, 2H), 7.62 (d, *J* = 8.2 Hz, 4H), 7.35 (d, *J* = 8.2 Hz, 4H), 3.95 (s, 4H). **^{13}C NMR** (63 MHz, CDCl$_3$) δ 161.5, 136.7, 134.6, 129.4, 129.0, 61.6.

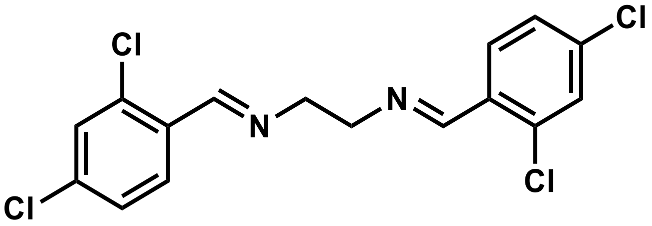


***N,N*'-(Ethane-1,2-diyl)*bis*(1-(3-chlorophenyl)methanimine) (2g).**[5] Yield: 1.08 g (3.5 mmol, 88%), white crystals, **MP:** 85-86 °C. **IR** (ATR, cm^{-1}): 1652, 1564, 1480, 1419, 1368, 1281, 1221, 1094, 1070, 1023, 973, 904, 872, 792, 731, 686. **^{1}H NMR** (250 MHz, CDCl$_3$) δ 8.18 (s, 2H), 7.68 (s, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 11.1 Hz, 4H), 3.93 (s, 4H). **^{13}C NMR** (63 MHz, CDCl$_3$) δ 161.3, 137.9, 134.9, 130.7, 129.9, 127.8, 126.6, 61.5.

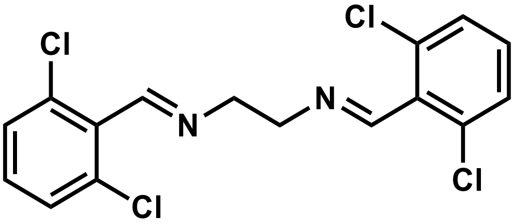


***N,N*'-(Ethane-1,2-diyl)*bis*(1-(2-chlorophenyl)methanimine) (2h).**[6] Yield: 1.00 g (2.4 mmol, 60%), white crystals, **MP:** 87-88 °C. **IR** (ATR, cm^{-1}): 1635, 1594, 1469, 1437, 1374, 1273, 1053, 1018, 967, 865, 759, 707. **^{1}H NMR** (250 MHz, CDCl$_3$) δ 8.73 (s, 2H), 8.01 (d, *J* = 7.5

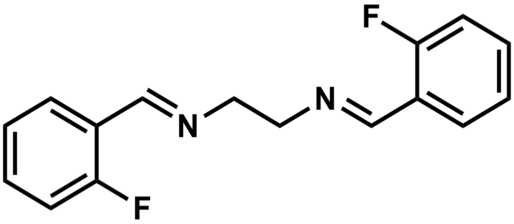
Hz, 2H), 7.36 – 7.23 (m, 6H), 4.03 (s, 4H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 159.7, 135.2, 133.3, 131.6, 129.8, 128.5, 127.1, 61.6.



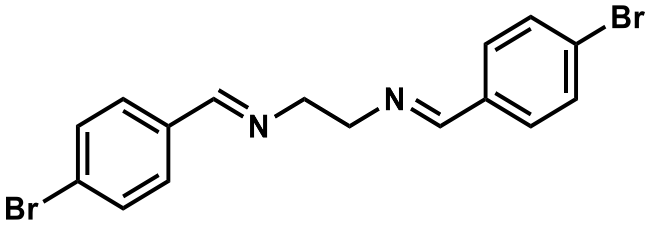
***N,N*'-(Ethane-1,2-diyl)*bis*(1-(2,4-dichlorophenyl)methanimine) (2i).** Yield: 1.32 g (3.5 mmol, 88%), white crystals, **MP:** 140-141 °C. **IR** (ATR, cm^{-1}): 1640, 1592, 1471, 1383, 1368, 1255, 1206, 1102, 1051, 1023, 962, 865, 837, 796, 768. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 8.53 (s, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.26 (s, 2H), 7.22 – 7.09 (m, 2H), 3.91 (s, 4H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 158.6, 137.1, 135.7, 131.8, 129.6, 129.4, 127.6, 61.5. **HRMS** (ESI, *m/z*) calcd for $C_{16}H_{13}N_2Cl_4$ ($M+H^+$): 372.9833, found: 372.9822.



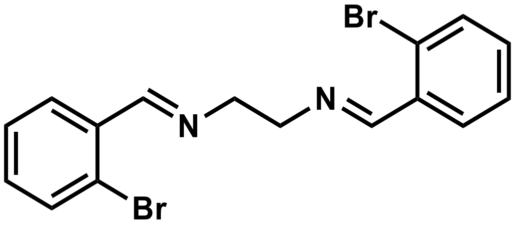
***N,N*'-(Ethane-1,2-diyl)*bis*(1-(2,6-dichlorophenyl)methanimine) (2j).**[7] Yield: 1.32 g (3.5 mmol, 88%), white crystals, **MP:** 148-149 °C. IR. (ATR, cm^{-1}): 1640, 1585, 1555, 1435, 1359, 1197, 1096, 1012, 947, 777, 725. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 8.55 (s, 2H), 7.35 (d, *J* = 7.8 Hz, 4H), 7.28 – 7.14 (m, 2H), 4.18 (s, 4H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 158.5, 134.8, 132.8, 130.3, 128.7, 62.2.



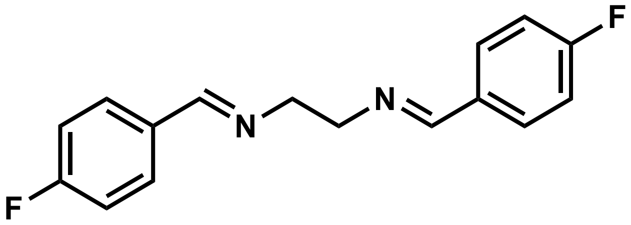
***N,N*'-(Ethane-1,2-diyl)*bis*(1-(2-fluorophenyl)methanimine) (2k).**[8] Yield: 0.60 g (2.0 mmol, 51%), white crystals, **MP:** 65-66 °C. **IR** (ATR, cm^{-1}): 1640, 1614, 1585, 1486, 1454, 1379, 1283, 1228, 1152, 1102, 1016, 969, 874, 811, 764. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 8.60 (s, 2H), 7.96 (t, *J* = 7.5 Hz, 2H), 7.37 (q, *J* = 7.0 Hz, 2H), 7.10 (dt, *J* = 28.6, 8.5 Hz, 4H), 4.00 (s, 4H). **^{13}C NMR** (63 MHz, CDCl$_3$) δ 162.8 (d, *J* = 252.1 Hz), 156.6 (d, *J* = 4.7 Hz), 132.8 (d, *J* = 8.6 Hz), 128.3 (d, *J* = 2.9 Hz), 124.9 (d, *J* = 3.7 Hz), 124.4 (d, *J* = 9.4 Hz), 116.3 (d, *J* = 21.1 Hz), 62.5.



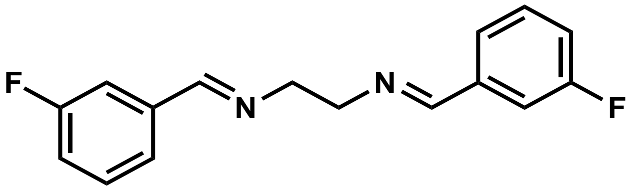
***N,N*'-(Ethane-1,2-diyl)*bis*(1-(4-bromophenyl)methanimine) (2l).**[5] Yield: 1.50 g (3.8 mmol, 95%), white crystals, **MP:** 155-156 °C. **IR** (ATR, cm^{-1}): 1642, 1588, 1488, 1374, 1070, 1010, 822. **^{1}H NMR** (250 MHz, CDCl$_3$) δ 8.20 (s, 2H), 7.65 – 7.44 (m, 8H), 3.94 (s, 4H). **^{13}C NMR** (63 MHz, CDCl$_3$) δ 161.54, 135.06, 131.92, 129.59, 125.18, 61.54.



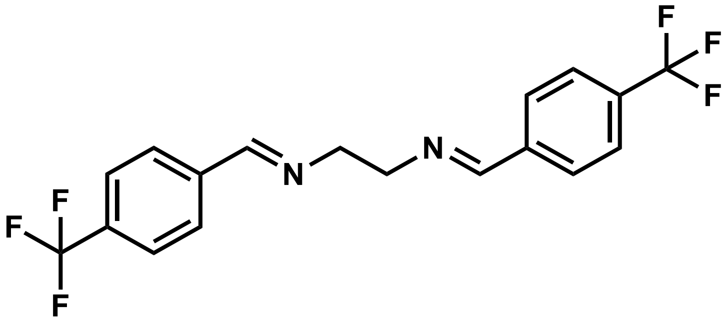
***N,N*'-(Ethane-1,2-diyl)*bis*(1-(2-bromophenyl)methanimine) (2m).**[9] Yield: 1.09 g (2.8 mmol, 69%), white crystals, **MP:** 97-98 °C. **IR** (ATR, cm^{-1}): 1633, 1596, 1432, 1374, 1269, 1014, 969, 764. **^{1}H NMR** (250 MHz, CDCl$_3$) δ 8.65 (s, 2H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.27 (dt, *J* = 21.5, 7.4 Hz, 4H), 4.04 (s, 4H). **^{13}C NMR** (63 MHz, CDCl$_3$) δ 162.4, 135.1, 133.5, 132.3, 129.4, 128.1, 125.6, 61.9.



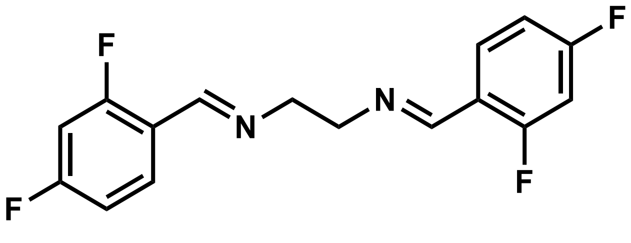
***N,N*'-(Ethane-1,2-diyl)*bis*(1-(4-fluorophenyl)methanimine) (2n).**[5] Yield: 0.77 g (2.8 mmol, 71%), white crystals, **MP:** 94-95 °C. **IR** (ATR, cm^{-1}): 1652, 1598, 1508, 1228, 1154, 1023, 846. **^{1}H NMR** (250 MHz, CDCl$_3$) δ 8.23 (s, 2H), 7.84 – 7.54 (m, 4H), 7.06 (t, *J* = 8.5 Hz, 4H), 3.94 (s, 4H). ^{13}**C NMR** (63 MHz, CDCl$_3$) δ 164.4 (d, *J* = 250.8 Hz), 161.3, 132.5 (d, *J* = 3.1 Hz), 130.1 (d, *J* = 8.6 Hz), 115.8 (d, *J* = 22.0 Hz), 61.6.



***N,N*'-(Ethane-1,2-diyl)*bis*(1-(3-fluorophenyl)methanimine) (2o).**[10] Yield: 0.81 g (3.0 mmol, 75%), white crystals, **MP:** 58-59 °C. **IR** (ATR, cm^{-1}): 1646, 1588, 1452, 1264, 785, 682. ^{1}**H NMR** (250 MHz, CDCl$_3$) δ 8.24 (s, 2H), 7.62 – 7.25 (m, 6H), 7.10 (d, *J* = 8.1 Hz, 2H), 3.97 (s, 4H). ^{13}**C NMR** (63 MHz, CDCl$_3$) δ 163.1 (d, *J* = 246.4 Hz), 161.4 (d, *J* = 3.0 Hz), 138.5 (d, *J* = 7.3 Hz), 130.2 (d, *J* = 8.0 Hz), 124.3 (d, *J* = 2.9 Hz), 117.7 (d, *J* = 21.5 Hz), 114.2 (d, *J* = 22.3 Hz), 61.4.

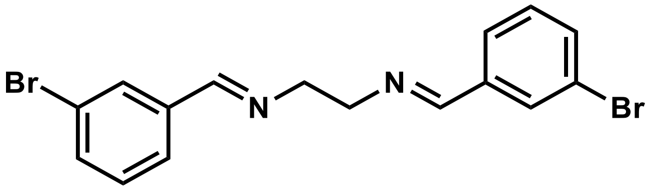


***N,N*'-(Ethane-1,2-diyl)*bis*(1-(4-(trifluoromethyl)phenyl)methanimine) (2p).**[11] Yield: 1.14 g (3.0 mmol, 76%), white crystals, **MP:** 116-118 °C. **IR** (ATR, cm^{-1}): 1650, 1419, 1322, 1312, 1161, 1132, 1107, 1064, 1020, 973, 954, 839, 740. ^{1}**H NMR** (250 MHz, CDCl$_3$) δ 8.32 (s, 2H), 7.80 (d, *J* = 7.7 Hz, 4H), 7.63 (d, *J* = 7.9 Hz, 4H), 4.03 (d, *J* = 5.1 Hz, 4H). ^{13}**C NMR** (63 MHz, CDCl$_3$) δ 161.3, 139.3, 132.4 (q, *J* = 32.4 Hz), 128.4, 125.7 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.3 Hz), 61.6.

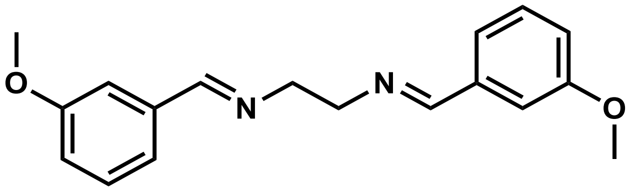


***N,N*'-(Ethane-1,2-diyl)*bis*(1-(2,4-difluorophenyl)methanimine) (2q).** Yield: 0.98 g (3.2 mmol, 79%), white crystals, **MP:** 112-113 °C. **IR** (ATR, cm^{-1}): 1635, 1283, 1145, 969, 837. ^{1}**H**

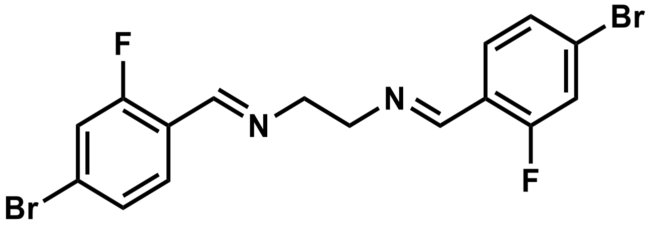
NMR (250 MHz, $CDCl_3$) δ 8.50 (s, 2H), 7.95 (q, *J* = 7.9 Hz, 2H), 6.83 (dt, *J* = 24.5, 9.2 Hz, 4H), 3.96 (s, 4H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 163.5 (dd, *J* = 122.1, 12.2 Hz), 163.5 (dd, *J* = 385.9, 12.4 Hz), 155.0 (d, *J* = 4.2 Hz), 129.2 (dd, *J* = 10.0, 4.5 Hz), 120.4 (dd, *J* = 9.6, 3.7 Hz), 112.1 (dd, *J* = 21.6, 3.7 Hz), 104.0 (t, *J* = 25.3 Hz), 61.8. **HRMS** (ESI, *m/z*) calcd for $C_{16}H_{13}N_2F_4$ (M+H$^+$): 309.1015, found: 309.1018.



***N,N*'-(Ethane-1,2-diyl)*bis*(1-(3-bromophenyl)methanimine) (2r).**[3] Yield: 1.03 g (2.6 mmol, 65%), white crystals, **MP:** 83-84 °C. **IR** (ATR, cm^{-1}): 1644, 1471, 1428, 1368, 1266, 1215, 1070, 1018, 964, 8989, 787, 686. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 8.20 (s, 2H), 7.88 (s, 2H), 7.54 (dd, *J* = 13.1, 7.4 Hz, 4H), 7.24 (t, *J* = 7.7 Hz, 2H), 3.96 (s, 4H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 161.7, 138.6, 134.1, 131.2, 130.7, 127.5, 123.5, 62.0.



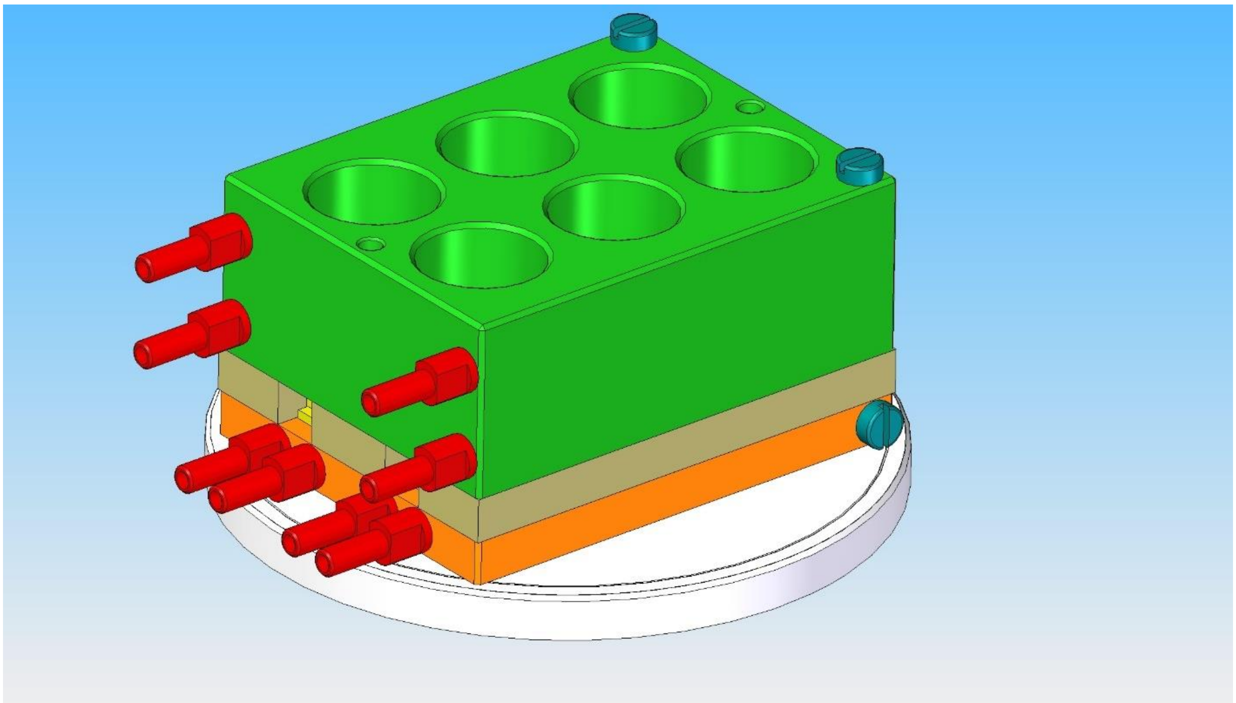
***N,N*'-(ethane-1,2-diyl)*bis*(1-(3-methoxyphenyl)methanimine) (2s).**[12] Yield: 0.63 g (2.1 mmol, 53%), off-wite crystals, **MP:** 54-55 °C. **IR** (ATR, cm^{-1}): 1644, 1588, 1489, 1469, 1435, 1381, 1324, 1269, 1158, 1044, 787, 693. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 8.24 (s, 2H), 7.44 – 7.12 (m, 6H), 6.95 (d, *J* = 7.9 Hz, 2H), 3.96 (s, 4H), 3.81 (s, 6H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 163.1, 160.4, 138.1, 130.1, 121.9, 117.9, 112.1, 62.1, 55.8.

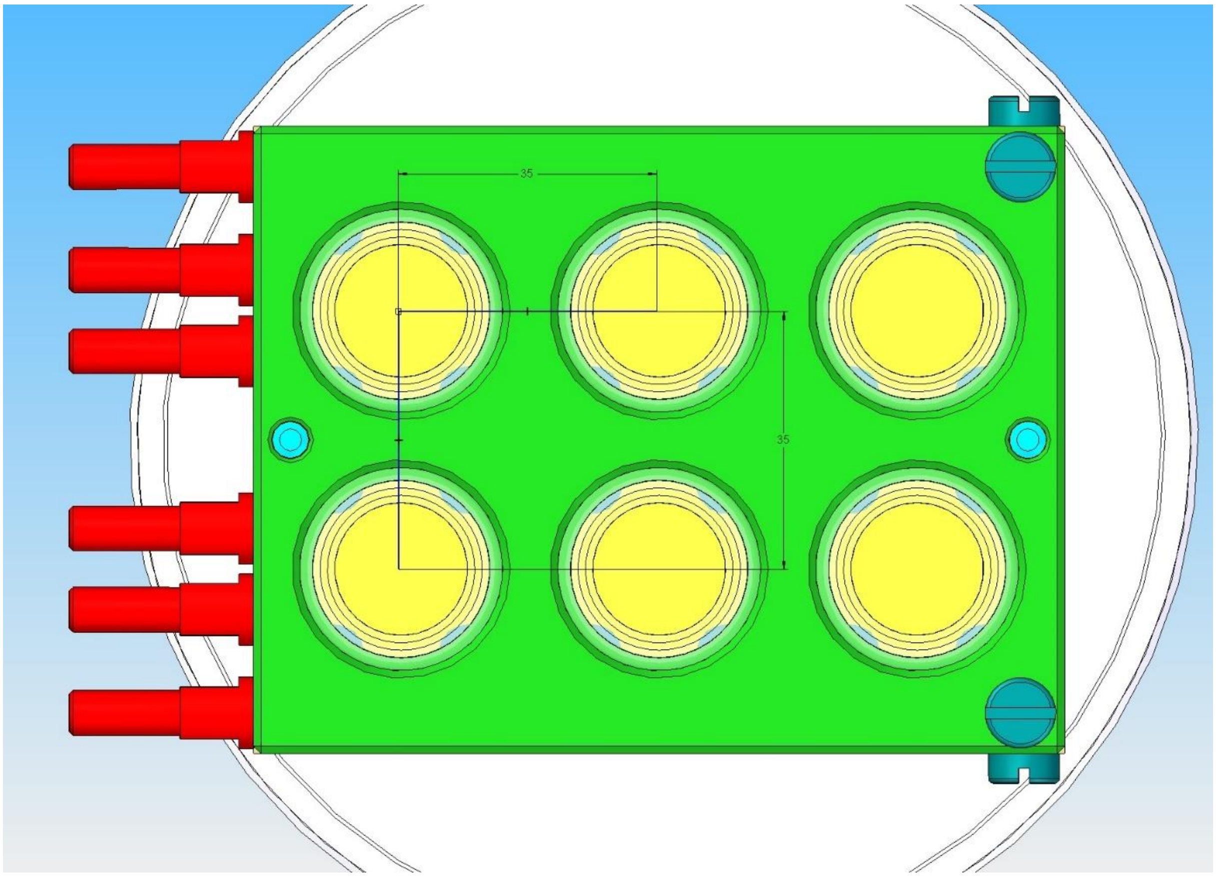


***N,N'*-(Ethane-1,2-diyl)*bis*(1-(4-bromo-2-fluorophenyl)methanimine) (2t).** Yield: 1.58 g (3.6 mmol, 91%), white crystals, **MP:** 164-165 °C. **IR** (ATR, cm^{-1}): 1644, 1603, 1571, 1484, 1461, 1404, 1381, 1284, 1268, 1186, 1113, 1066, 1023, 973, 889, 841, 815. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 8.27 (s, 2H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.04 (dd, *J* = 12.4, 8.4 Hz, 4H), 3.74 (s, 4H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 161.8 (d, *J* = 256.8 Hz), 155.2 (d, *J* = 4.4 Hz), 128.9 (d, *J* = 3.6 Hz), 128.0 (d, *J* = 3.6 Hz), 125.3 (d, *J* = 9.7 Hz), 122.9 (d, *J* = 9.6 Hz), 119.5 (d, *J* = 24.5 Hz), 61.8. **HRMS** (ESI, *m/z*) calcd for $C_{16}H_{13}N_2F_2Br_2$ (M+H$^+$): 428.9414, found: 428.9405.

The arrangement of our photoreactor

The 6-vial photoreactor has been assembled from two temperature-adjustable part. There is a lower LED panel (orange) housing the 10W LEDs (yellow) and the upper vial holder block (green). The reactor seated on the plate of magnetic stirrer (white) assuring the good mixing. All elements made of aluminum, and the 20 mL glass vials fit into the nests precociously to achieve the homogenic temperature profile. The LEDs shine from bellow through the glass and solutions. The distance between the light sources and vials is 10 mm. The internal (reaction) temperature measured in the vial, using digital thermometer, and controlled by Julabo CD-300F thermostat (through the red spouts).

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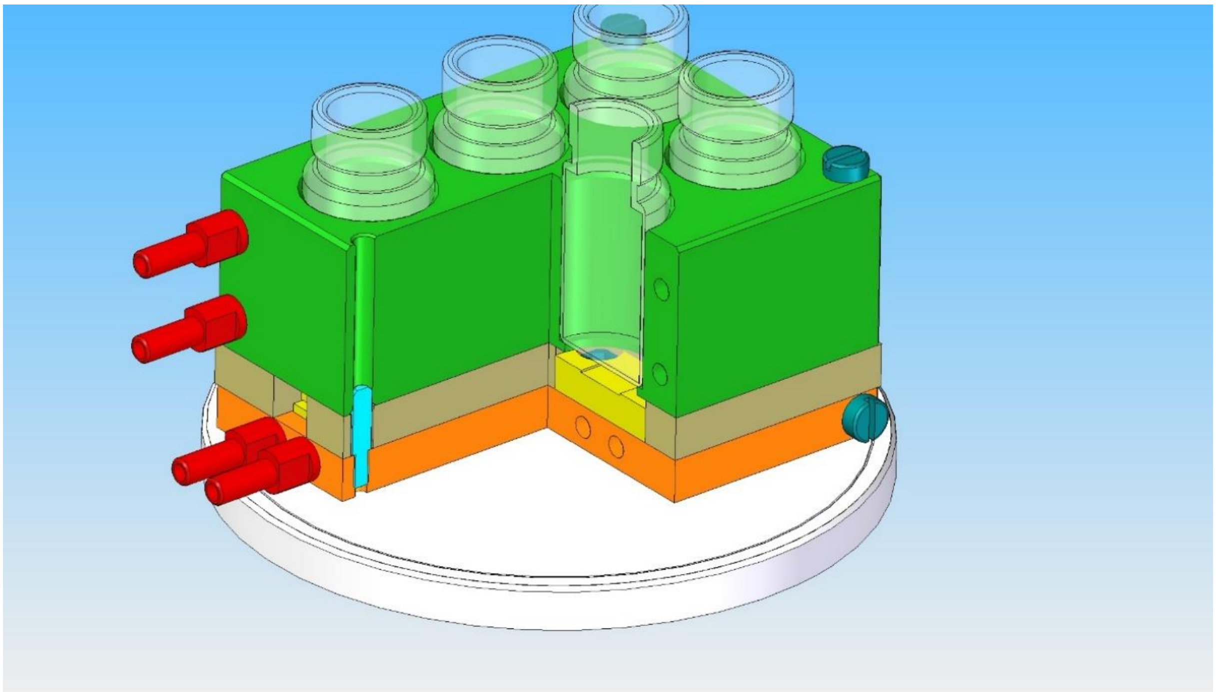
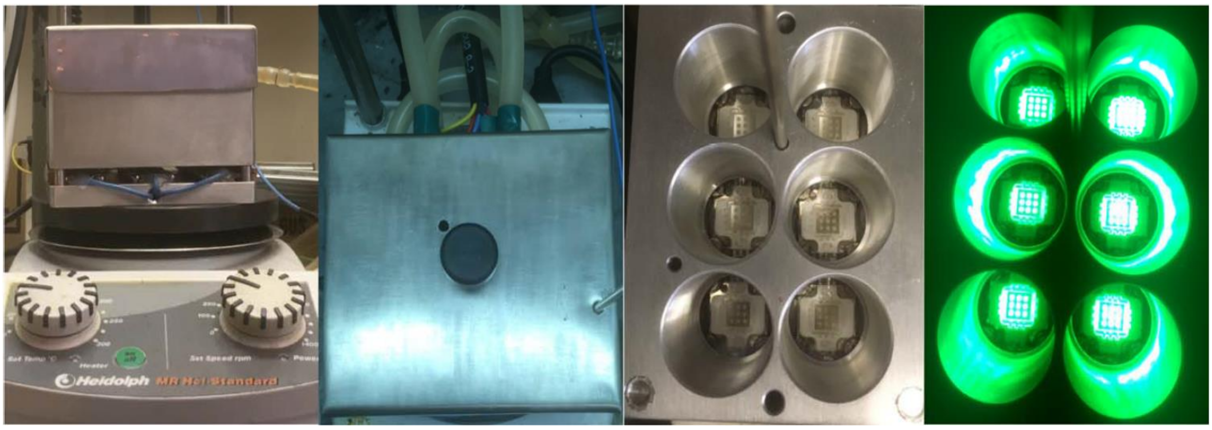
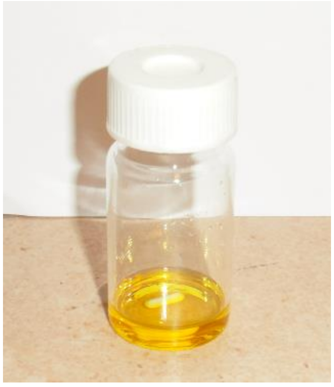


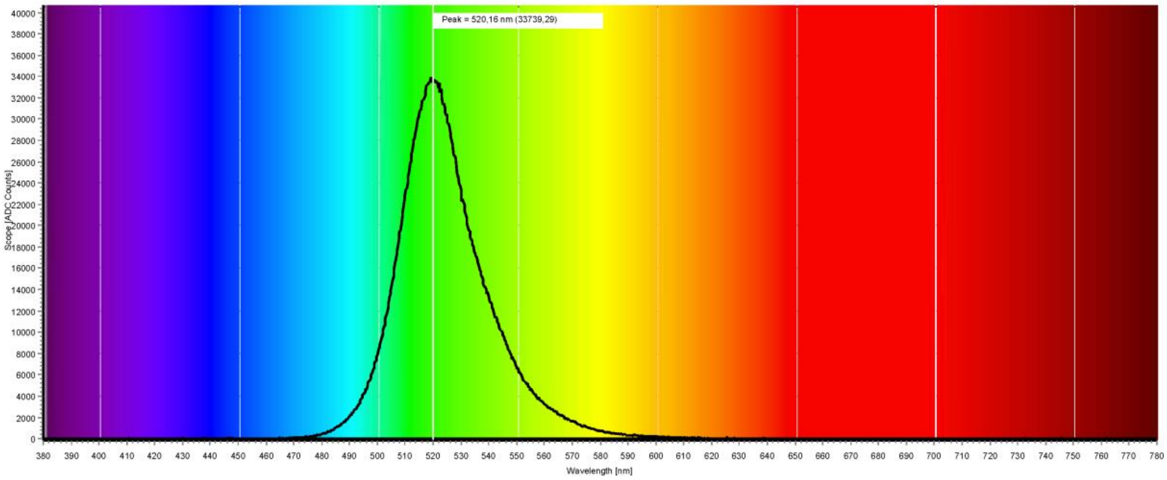




Operating LEDs

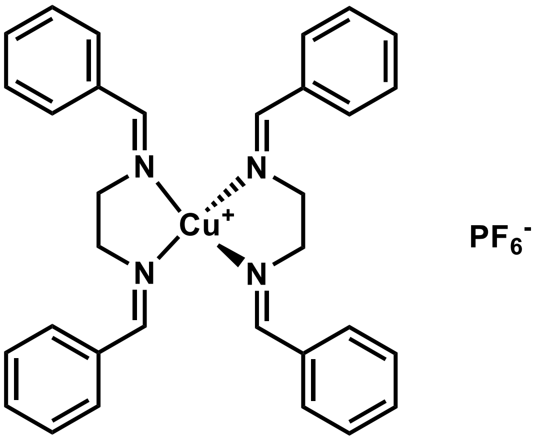
Green LED parameters: 10W High power COB-LED chips, Green 520-525nm (8.0-10V, 840-1000mA, 600-800LM) operates 3 in series circuit connected to current generator: AC 100-260V in, DC 20-40V 900mA 30W out.

Measured emission spectrum of green LEDs.

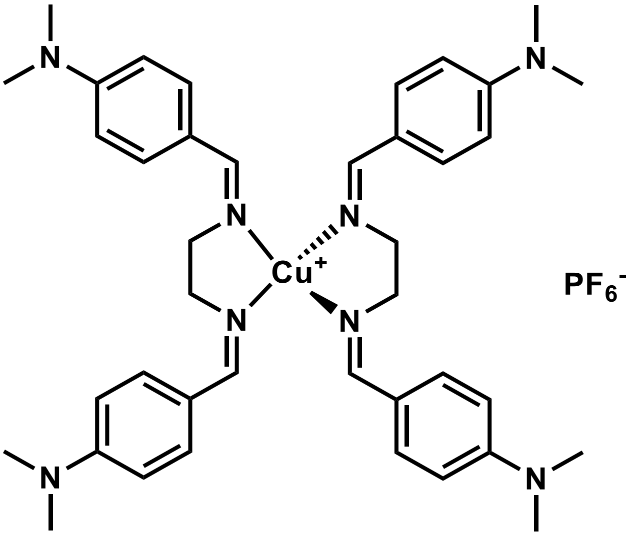


General procedure for preparation of copper complexes

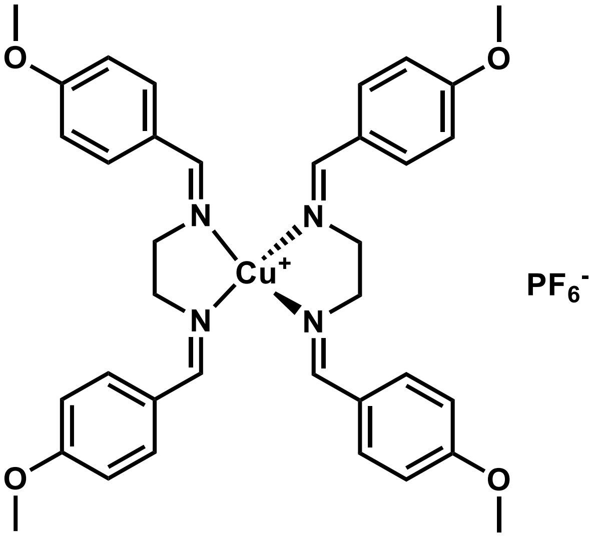
Diimine ligand (**2**, 0.4 mmol) and *tetrakis*(acetonitrile)copper(I) hexafluorophosphate (75 mg, 0.2 mmol) were dissolved in absolute DCM (30 mL) using a Schlenk flask under argon atmosphere. The reaction mixture was stirred at 25°C for 3-4 h. Then diethyl ether (15 mL) was added and the resultant mixture was stirred at 25°C for a further 30 min. The precipitate was filtered and washed with diethyl ether, finally dried *in vacuo*. If no precipitate formed, the volume of the reaction mixture was reduced to approximately one third, then another portion of diethyl ether was added and stirred for 20-30 min. The precipitate was filtered and washed with diethyl ether, finally dried *in vacuo*. The products obtained were used in the next step without further purification.



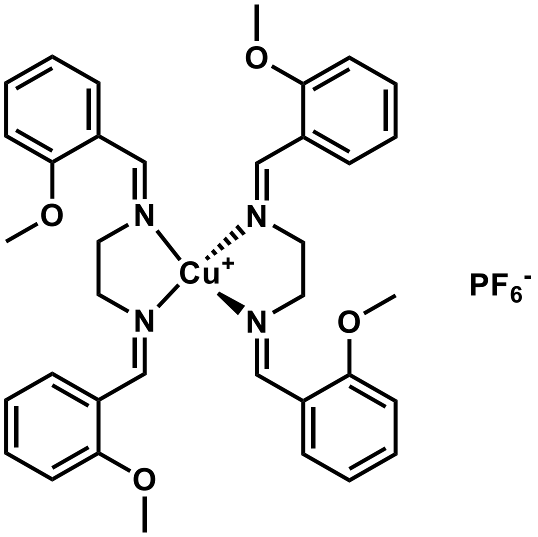
***bis*[*N*,*N*'-(Ethane-1,2-diyl)*bis*(1-phenylmethaniminyl)]copper(I) hexafluorophosphate (6a).** Yield: 109 mg (0.16 mmol, 80%), yellow crystals, **MP:** 214-215 °C. **IR** (ATR, cm^{-1}): 1629, 1439, 1350, 1318, 1227, 1042, 956, 856, 830, 755, 693. **^{1}H NMR** (250 MHz, DMSO-d_6) δ 8.58 (s, 4H), 7.71 (d, *J* = 7.4 Hz, 8H), 7.58 – 7.30 (m, 12H), 4.00 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-d_6) δ 164.9, 133.9, 131.8, 128.4, 128.3, 60.7. **HRMS** (ESI, *m/z*) calcd for $C_{32}H_{32}N_4Cu$ (M$^+$): 535.1923, found: 535.1914. UV-VIS (2.0 mg/10mL CH_2Cl_2): λ_{max} = 409 nm (32).



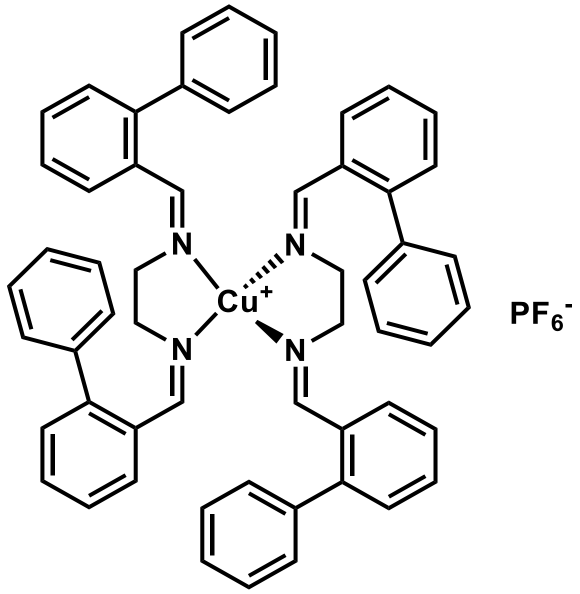
***bis*[4,4'-((Ethane-1,2-diylbis(azaneylylidene))*bis*(methaneylylidene))*bis*(*N*,*N*-dimethylanilinyl)]copper(I) hexafluorophosphate (6b).** Yield: 128 mg (0.15 mmol, 75%), yellow crystals, **MP:** 193-194 °C. **IR** (ATR, cm^{-1}): 1599, 1527, 1439, 1376, 1322, 1188, 949, 843. **^{1}H NMR** (250 MHz, Acetone-*d*$_6$) δ 8.38 (s, 4H), 7.84 (d, *J* = 8.7 Hz, 8H), 6.70 (d, *J* = 8.8 Hz, 8H), 4.10 (s, 8H), 2.99 (s, 24H). **^{13}C NMR** (63 MHz, Acetone-*d*$_6$) δ 164.6, 153.9, 131.7, 123.0, 111.9, 62.5, 40.2. **HRMS** (ESI, *m/z*) calcd for $C_{40}H_{52}N_8Cu$ (M^+): 707.3611, found: 707.3631. UV-VIS (2.5 mg/10mL CH_2Cl_2): λ_{max} = 437 nm (64).



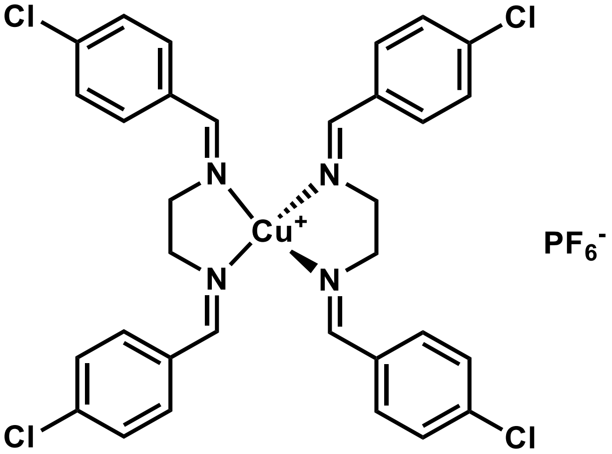
***bis*[*N*,*N'*-(Ethane-1,2-diyl)*bis*(1-(4-methoxyphenyl)methaniminyl)]copper(I) hexafluorophosphate (6c).** Yield: 136 mg (0.17 mmol, 86%), greenish yellow crystals, **MP:** 187-189 °C. **IR** (ATR, cm^{-1}): 1629, 1601, 1516, 1314, 1260, 1173, 1025, 843. **^{1}H NMR** (250 MHz, Acetone-*d*$_6$) δ 8.52 (d, *J* = 5.3 Hz, 4H), 7.85 (d, *J* = 7.9 Hz, 8H), 6.99 (d, *J* = 7.8 Hz, 8H), 4.14 (d, *J* = 5.4 Hz, 8H), 3.82 (d, *J* = 5.1 Hz, 12H). **^{13}C NMR** (63 MHz, Acetone-*d*$_6$) δ 165.3, 163.7, 131.6, 128.0, 114.8, 62.3, 56.0. **HRMS** (ESI, *m/z*) calcd for $C_{36}H_{40}N_4O_4Cu$ (M^+): 655.2346, found: 655.2349. UV-VIS (2.4 mg/10mL CH_2Cl_2): λ_{max} = 410 nm (43).



***bis*[*N*,*N*'-(Ethane-1,2-diyl)*bis*(1-(2-methoxyphenyl)methaniminyl)]copper(I) hexafluorophosphate (6d).** Yield: 149 mg (0.18 mmol, 92%), yellow crystals, **MP:** 194-196 °C. **IR** (ATR, cm^{-1}): 1626, 1603, 1489, 1469, 1437, 1393, 1307, 1255, 1167, 1113, 1020, 841. **^{1}H NMR** (250 MHz, DMSO-d_6) δ 8.65 (s, 4H), 7.78 (d, *J* = 7.6 Hz, 4H), 7.45 (t, *J* = 7.9 Hz, 4H), 6.96 (dd, *J* = 18.0, 8.4 Hz, 8H), 3.87 (s, 8H), 3.73 (s, 12H). **^{13}C NMR** (63 MHz, DMSO-d_6) δ 159.9, 158.4, 133.2, 127.0, 119.6, 111.4, 60.9, 55.5. **HRMS** (ESI, *m/z*) calcd for $C_{36}H_{40}N_4O_4Cu$ (M^+): 655.2346, found: 655.2357. UV-VIS (2.4 mg/10mL CH_2Cl_2): λ_{max} = 410 nm (55).

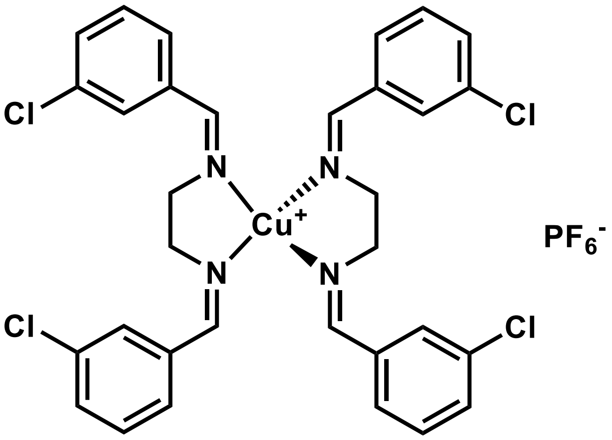


***bis*[*N*,*N*'-(Ethane-1,2-diyl)*bis*(1-([1,1'-biphenyl]-2-yl)methaniminyl)]copper(I) hexafluorophosphate (6e).** Yield: 182 mg (0.19 mmol, 94%), yellow crystals, **MP:** 247-249 °C. **IR** (ATR, cm^{-1}): 1635, 1279, 841. **^{1}H NMR** (250 MHz, DMSO-d_6) δ 8.27 (d, J = 7.7 Hz, 4H), 8.17 (s, 4H), 7.80 (d, J = 7.8 Hz, 4H), 7.65 (d, J = 8.0 Hz, 4H), 7.50 – 7.13 (m, 16H), 6.51 (d, J = 7.3 Hz, 8H), 3.92 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-d_6) δ 162.9, 143.0, 137.8, 131.8, 131.6, 130.4, 129.5, 128.4, 127.9, 127.4, 127.0, 60.6. **HRMS** (ESI, *m/z*) calcd for $C_{56}H_{48}N_4Cu$ (M^+): 839.3175, found: 839.3194. UV-VIS (3.0 mg/10mL CH_2Cl_2): λ_{max} = 426 nm (45).

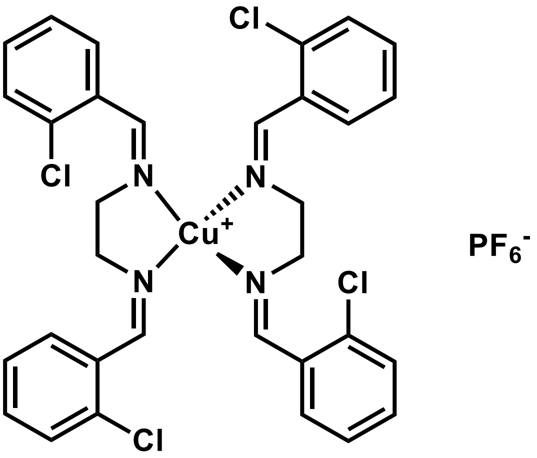


***bis*[*N*,*N*'-(ethane-1,2-diyl)*bis*(1-(4-chlorophenyl)methaniminyl]copper(I) hexafluorophosphate (6f).** Yield: 151 mg (0.18 mmol, 92%), bright yellow crystals, **MP:** 232-234 °C. **IR** (ATR, cm^{-1}): 1642, 1092, 841. **^{1}H NMR** (250 MHz, DMSO-d_6) δ 8.59 (s, 4H), 7.68 (d, J = 8.1 Hz, 8H), 7.54 (d, J = 8.1 Hz, 8H), 4.01 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-d_6) δ

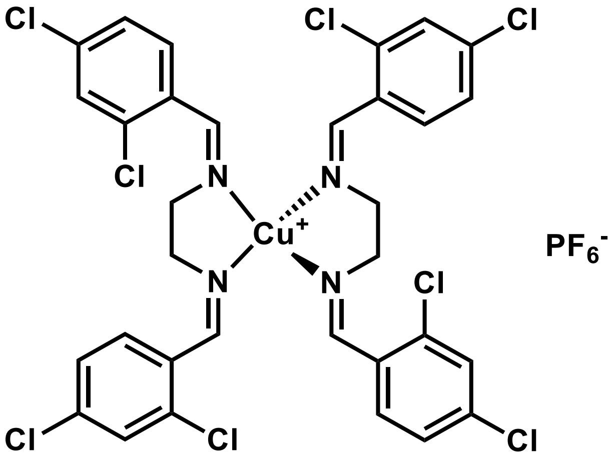
164.1, 136.4, 132.6, 129.9, 128.7, 60.8. **HRMS** (ESI, *m/z*) calcd for $C_{32}H_{28}N_4Cl_4Cu$ (M^+): 671.0364, found: 671.0370. UV-VIS (2,5 mg/10 mL CH_2Cl_2): λ_{max} = 410 nm (47).



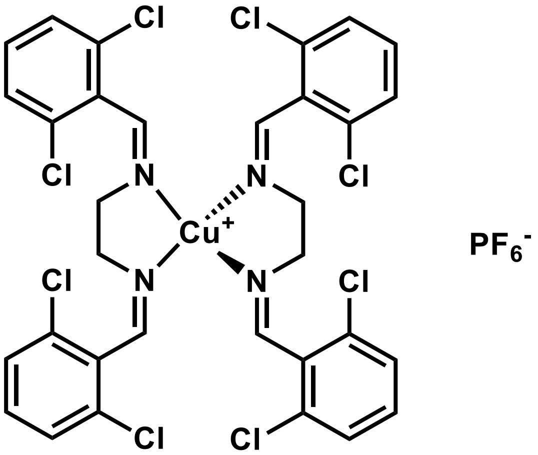
***bis*[*N,N'*-(Ethane-1,2-diyl)*bis*(1-(3-chlorophenyl)methaniminyl)]copper(I) hexafluorophosphate (6g).** Yield: 87 mg (0.11 mmol, 53%), bright yellow crystals, **MP:** 195-198 °C. **IR** (ATR, cm^{-1}): 1633, 1221, 841, 684. **^{1}H NMR** (250 MHz, DMSO-*d₆*) δ 8.67 (s, 4H), 7.75 (s, 4H), 7.51 (d, *J* = 25.7 Hz, 12H), 4.06 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-*d₆*) δ 164.3, 135.7, 133.3, 131.6, 130.7, 127.8, 126.5, 60.8. **HRMS** (ESI, *m/z*) calcd for $C_{32}H_{28}N_4Cl_4Cu$ (M^+): 671.0364, found: 671.0366. UV-VIS (2.5 mg/10 mL CH_2Cl_2): λ_{max} = 407 nm (39).



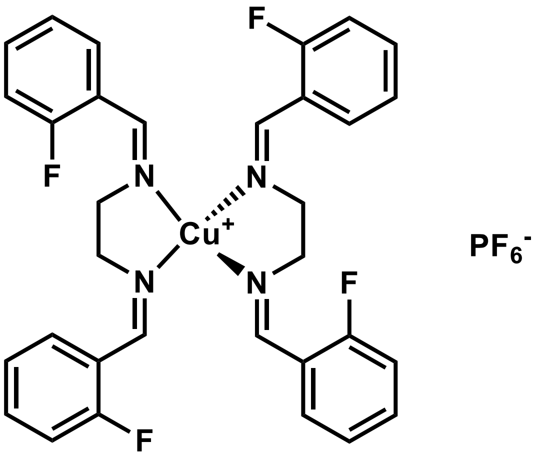
***bis*[*N,N'*-(Ethane-1,2-diyl)*bis*(1-(2-chlorophenyl)methaniminyl)]copper(I) hexafluorophosphate (6h).** Yield: 148 mg (0.18 mmol, 89%), orange crystals, **MP:** 230-232 °C. **IR** (ATR, cm^{-1}): 1633, 1443, 1346, 1040, 835, 759. **^{1}H NMR** (250 MHz, DMSO-*d₆*) δ 8.66 (s, 4H), 7.77 (d, *J* = 7.4 Hz, 4H), 7.46 (d, *J* = 10.7 Hz, 12H), 3.90 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-*d₆*) δ 161.2, 133.9, 133.1, 131.6, 129.8, 128.3, 126.9, 60.5. **HRMS** (ESI, *m/z*) calcd for $C_{32}H_{28}N_4Cl_4Cu$ (M^+): 671.0364, found: 671.0364. UV-VIS (2.5 mg/10 mL CH_2Cl_2): λ_{max} = 405 nm (53).



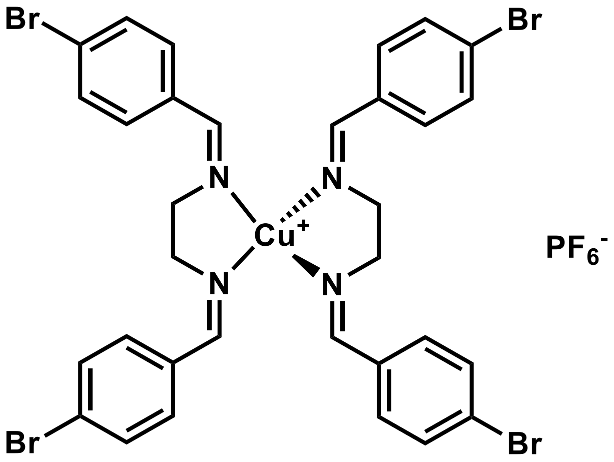
***bis*[*N*,*N'*-(Ethane-1,2-diyl)*bis*(1-(2,4-dichlorophenyl)methaniminyl)]copper(I) hexafluorophosphate (6i).** Yield: 184 mg (0.19 mmol, 95%), yellow crystals, **MP:** 248-250 °C (decomp). **IR** (ATR, cm^{-1}): 1644, 1104. **^{1}H NMR** (250 MHz, DMSO-d_6) δ 8.64 (s, 4H), 7.74 (d, *J* = 8.4 Hz, 4H), 7.69 – 7.46 (m, 8H), 4.04 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-d_6) δ 160.4, 137.2, 134.8, 129.9, 129.5, 129.3, 127.4, 61.1. **HRMS** (ESI, *m/z*) calcd for $C_{32}H_{24}N_4Cl_8Cu$ (M^+): 806.8805, found: 806.8815. UV-VIS (2.8 mg/10 mL CH_2Cl_2): λ_{max} = 410 nm (35).



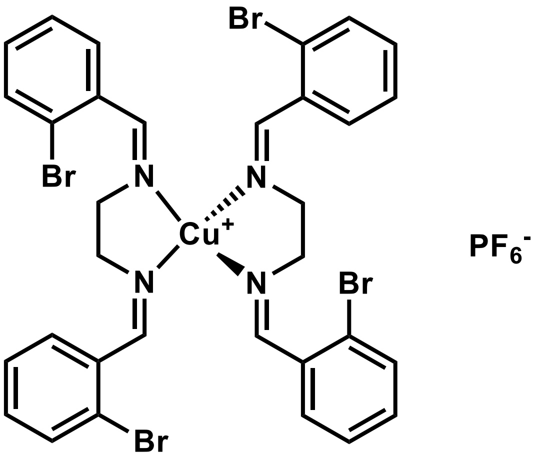
***bis*[*N*,*N'*-(Ethane-1,2-diyl)*bis*(1-(2,6-dichlorophenyl)methaniminyl)]copper(I) hexafluorophosphate (6j).** Yield: 180 mg (0.19 mmol, 93%), yellow crystals, **MP:** 198-200 °C. **IR** (ATR, cm^{-1}): 1644, 1434, 1206, 1100, 843, 781. **^{1}H NMR** (500 MHz, DMSO-*d*6) δ 8.54 (s, 4H), 7.51 (d, *J* = 7.8 Hz, 8H), 7.43 (dd, *J* = 8.7, 7.3 Hz, 4H), 3.98 (s, 8H). **^{13}C NMR** (126 MHz, DMSO-*d*6, DEPT135) δ 133.4, 133.4, 131.5, 131.4, 128.9, 61.1. **HRMS** (ESI, *m/z*) calcd for $C_{32}H_{24}N_4Cl_8Cu$ (M^+): 806.8805, found: 806.8809. UV-VIS (2.8 mg/10 mL CH_2Cl_2): λ_{max} = 406 nm (25).



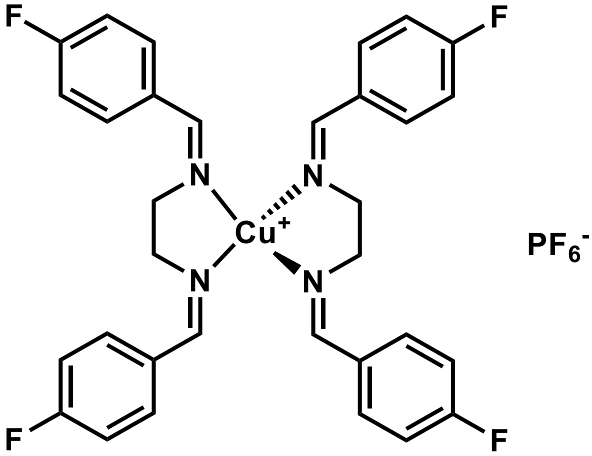
***bis*[*N*,*N*'-(Ethane-1,2-diyl)*bis*(1-(2-fluorophenyl)methaniminyl)]copper(I) hexafluorophosphate (6k).** Yield: 133 mg (0.18 mmol, 88%), yellow crystals, **MP:** 219-221 °C. **IR** (ATR, cm^{-1}): 1633, 1622, 1488, 1463, 1450, 1307, 1290, 1234, 1202, 836, 762. **^{1}H NMR** (250 MHz, DMSO-*d*$_6$) δ 8.61 (s, 4H), 7.79 (t, *J* = 7.6 Hz, 4H), 7.58 (q, *J* = 7.2 Hz, 4H), 7.40 – 7.08 (m, 8H), 3.98 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-*d*$_6$) δ 160.9 (d, *J* = 252.6 Hz), 158.3 (d, *J* = 5.1 Hz), 133.9 (d, *J* = 8.7 Hz), 127.5, 124.06, 121.7 (d, *J* = 10.4 Hz), 115.7 (d, *J* = 20.5 Hz), 60.8. **HRMS** (ESI, *m/z*) calcd for $C_{32}H_{28}N_4F_4Cu$ (M^+): 607.1546, found: 607.1546. UV-VIS (2.3 mg/10 mL CH_2Cl_2): λ_{max} = 407 nm (38).



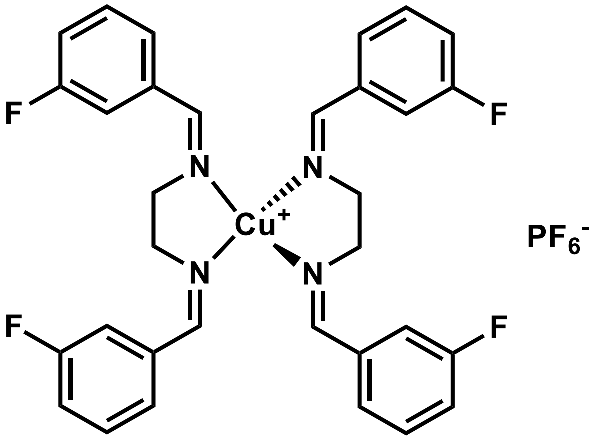
***bis*[*N*,*N*'-(Ethane-1,2-diyl)*bis*(1-(4-bromophenyl)methaniminyl)]copper(I) hexafluorophosphate (6l).** Yield: 182 mg (0.18 mmol, 91%), bright yellow crystals, **MP:** 242-245 °C. **IR** (ATR, cm^{-1}): 1635, 1488, 1070, 1014, 841. **^{1}H NMR** (250 MHz, DMSO-*d*$_6$) δ 8.58 (s, 4H), 7.68 (d, *J* = 8.1 Hz, 8H), 7.61 (d, *J* = 8.4 Hz, 8H), 4.00 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-*d*$_6$) δ 164.2, 132.9, 131.6, 130.0, 125.4, 60.8. **HRMS** (ESI, *m/z*) calcd for $C_{32}H_{28}N_4Br_4Cu$ (M^+): 846.8343, found: 846.8356. UV-VIS (2.9 mg/10mL CH_2Cl_2): λ_{max} = 410 nm (48).



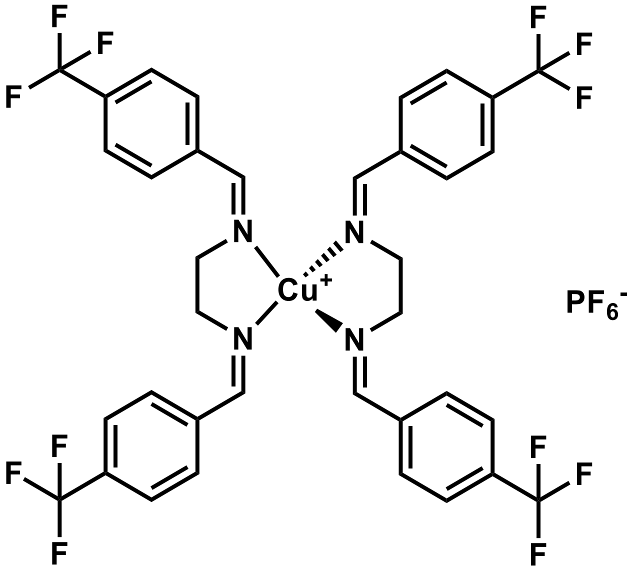
bis**[*****N*****,*****N*****'-(Ethane-1,2-diyl)*****bis*****(1-(2-bromophenyl)methaniminyl)]copper(I) hexafluorophosphate (6m).** Yield: 147 mg (0.15 mmol, 74%), orange crystals, **MP:** 235 °C (decomp). **IR** (ATR, cm^{-1}): 1631, 1443, 844, 759. **^{1}H NMR** (250 MHz, DMSO-*d$_6$*) δ 8.59 (s, 4H), 7.69 (dd, *J* = 14.9, 7.3 Hz, 8H), 7.47 (s, 8H), 3.85 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-*d$_6$*) δ 163.2, 133.3, 133.1, 128.6, 127.5, 123.9, 60.3. **HRMS** (ESI, *m/z*) calcd for $C_{32}H_{28}N_4Br_4Cu$ (M$^+$): 846.8343, found: 846.8336. UV/Vis (2.9 mg/10mL CH_2Cl_2): λ_{max} = 404 nm (59).



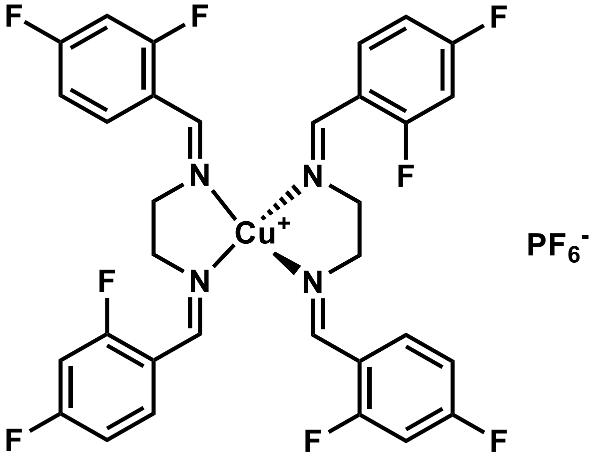
bis**[*****N*****,*****N*****'-(Ethane-1,2-diyl)*****bis*****(1-(4-fluorophenyl)methaniminyl)]copper(I) hexafluorophosphate (6n).** Yield: 119 mg (0.15 mmol, 78%), yellow crystals, **MP:** 235-237 °C. **IR** (ATR, cm^{-1}): 1633, 1603, 1512, 1236, 1161, 844. **^{1}H NMR** (250 MHz, DMSO-*d$_6$*) δ 8.55 (s, 4H), 7.71 (t, *J* = 7.1 Hz, 8H), 7.28 (t, *J* = 8.6 Hz, 8H), 4.00 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-*d$_6$*) δ 163.9, 163.9 (d, *J* = 250.7 Hz), 130.7 (d, *J* = 9.0 Hz), 130.5, 115.6 (d, *J* = 22.1 Hz), 60.8. **HRMS** (ESI, *m/z*) calcd for $C_{32}H_{28}N_4F_4Cu$ (M$^+$): 607.1546, found: 607.1550. UV-VIS (2.3 mg/10 mL CH_2Cl_2): λ_{max} = 407 nm (35).



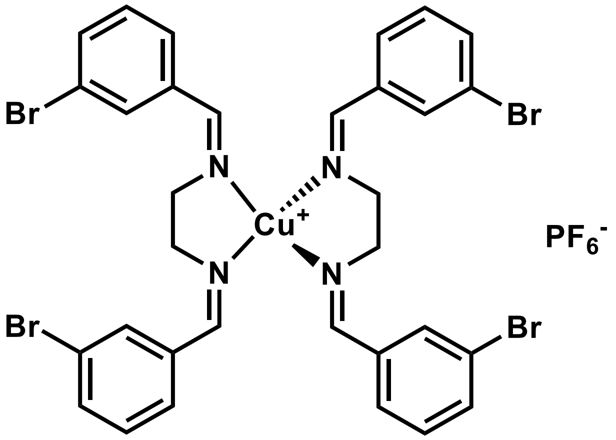
***bis*[*N,N*'-(Ethane-1,2-diyl)*bis*(1-(3-fluorophenyl)methaniminyl)]copper(I) hexafluorophosphate (6o).** Yield: 147 mg (0.19 mmol, 96%), yellow crystals, **MP:** 184-196 °C. **IR** (ATR, cm^{-1}): 1633, 1585, 1484, 1454, 1346, 1264, 1148, 843, 688. **^{1}H NMR** (250 MHz, DMSO-*d*$_6$) δ 8.64 (s, 4H), 7.42 (d, *J* = 24.7 Hz, 16H), 4.02 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-*d*$_6$) δ 164.3, 161.8 (d, *J* = 244.6 Hz), 136.1 (d, *J* = 7.6 Hz), 130.8 (d, *J* = 8.1 Hz), 124.8, 118.7 (d, *J* = 21.2 Hz), 114.0 (d, *J* = 22.6 Hz), 60.6. **HRMS** (ESI, *m/z*) calcd for $C_{32}H_{28}N_4F_4Cu$ (M^+): 607.1546, found: 607.1551. UV-VIS (2.3 mg/10 mL CH_2Cl_2): λ_{max} = 407 nm (39).



***bis*[*N,N*'-(Ethane-1,2-diyl)*bis*(1-(4-(trifluoromethyl)phenyl)methaniminyl)]copper(I) hexafluorophosphate (6p).** Yield: 174 mg (0.18 mmol, 90%), yellow crystals, **MP:** 258-260 °C. **IR** (ATR, cm^{-1}): 1631, 1325, 1165, 1128, 1066, 846, 830. **^{1}H NMR** (250 MHz, DMSO-*d*$_6$) δ 8.70 (s, 4H), 7.81 (s, 16H), 4.08 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-*d*$_6$) δ 164.4, 137.3, 121.6 (q, *J* = 272.9 Hz), 128.8, 125.5 (t, *J* = 4.2 Hz), 123.8 (q, *J* = 272.9 Hz), 61.0. **HRMS** (ESI, *m/z*) calcd for $C_{36}H_{28}N_4F_{12}Cu$ (M^+): 807.1418, found: 807.1433. UV-VIS (2.8 mg/10mL CH_2Cl_2): λ_{max} = 409 nm (42).

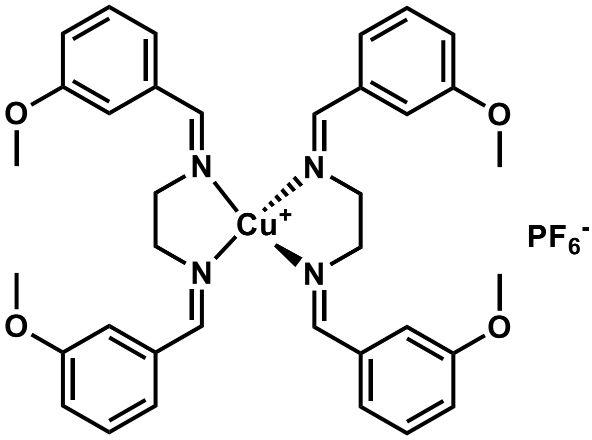


***bis*[*N*,*N*'-(Ethane-1,2-diyl)*bis*(1-(2,4-difluorophenyl)methaniminyl)]copper(I) hexafluorophosphate (6q).** Yield: 144 mg (0.17 mmol, 87%), yellow crystals, **MP:** 246-248 °C. **IR** (ATR, cm^{-1}): 1635, 1283, 1145, 969, 837. **^{1}H NMR** (250 MHz, DMSO-d_6) δ 8.57 (s, 4H), 7.77 (s, 4H), 7.26 (d, J = 9.5 Hz, 8H), 4.03 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-d_6) δ 167.3 – 158.6 (m), 157.6, 129.5 (d, J = 9.6 Hz), 118.5 (d, J = 10.2 Hz), 111.9 (d, J = 22.0 Hz), 104.4 (t, J = 25.6 Hz), 61.1. **HRMS** (ESI, *m/z*) calcd for $C_{32}H_{24}N_4F_8Cu$ (M^+): 679.1169, found: 679.1180. UV-VIS (2.5 mg/10mL CH_2Cl_2): λ_{max} = 408 nm (33).

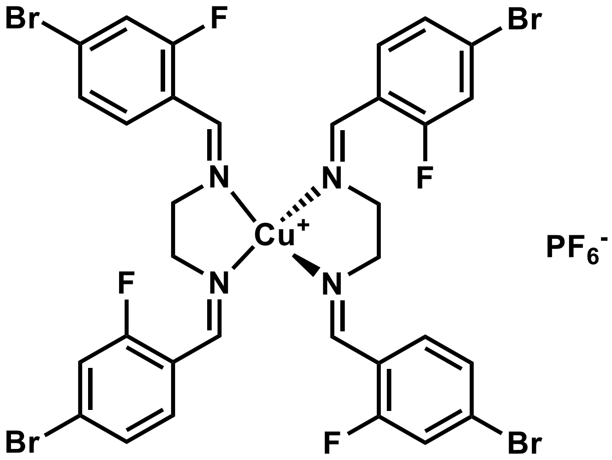


***bis*[*N*,*N*'-(Ethane-1,2-diyl)*bis*(1-(3-bromophenyl)methaniminyl)]copper(I) hexafluorophosphate (6r).** Yield: 181 mg (0.18 mmol, 91%), yellow crystals, **MP:** 188-191 °C. **IR** (ATR, cm^{-1}): 1629, 1562, 1471, 1348, 1212, 1074, 839, 684. **^{1}H NMR** (250 MHz, DMSO-d_6) δ 8.69 (s, 4H), 7.91 (s, 4H), 7.79 – 7.53 (m, 8H), 7.42 (s, 4H), 4.08 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-d_6) δ 164.4, 135.8, 134.5, 130.9, 129.1, 128.4, 121.9, 60.8. **HRMS**

(ESI, *m/z*) calcd for $C_{32}H_{28}N_4Br_4Cu$ (M^+): 846.8343, found: 846.8357. UV-VIS (2.9 mg/10mL CH_2Cl_2): λ_{max} = 407 nm (35).



***bis*[*N,N'*-(ethane-1,2-diyl)*bis*(1-(3-methoxyphenyl)methaniminyl)]copper(I) hexafluorophosphate (6s).** Yield: 137 mg (0.17 mmol, 85%), yellow crystals, **MP:** 100-104 °C. **IR** (ATR, cm^{-1}): 1631, 1585, 1463, 1279, 1161, 1050, 844, 692. **^{1}H NMR** (250 MHz, DMSO-*d*$_6$) δ 8.53 (s, 4H), 7.53 – 7.17 (m, 12H), 7.09 (d, *J* = 7.7 Hz, 4H), 3.97 (s, 8H), 3.74 (s, 12H). **^{13}C NMR** (63 MHz, DMSO-*d*$_6$) δ 164.7, 159.2, 135.4, 129.6, 120.4, 116.6, 114.3, 60.4, 55.4. **HRMS** (ESI, *m/z*) calcd for $C_{36}H_{40}N_4O_4Cu$ (M^+): 655.2346, found: 655.2347. UV-VIS (2.4 mg/10mL CH_2Cl_2): λ_{max} = 408 nm (37).

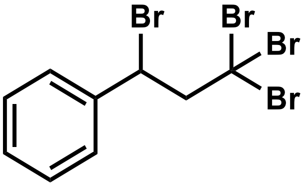


***bis*[*N,N'*-(Ethane-1,2-diyl)*bis*(1-(4-bromo-2-fluorophenyl)methaniminyl)]copper(I) hexafluorophosphate (6t).** Yield: 175 mg (0.16 mmol, 81%), orange crystals, **MP:** 230-231 °C. **IR** (ATR, cm^{-1}): 1640, 1484, 1413, 884, 835. **^{1}H NMR** (250 MHz, DMSO-*d*$_6$) δ 8.60 (s, 4H), 7.72 – 7.47 (m, 12H), 4.02 (s, 8H). **^{13}C NMR** (63 MHz, DMSO-*d*$_6$) δ 162.6, 158.5, 157.8

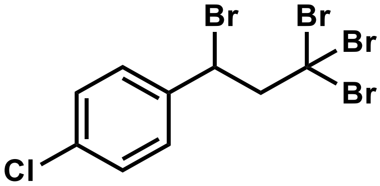
(d, J = 4.8 Hz), 128.2 (d, J = 84.9 Hz), 126.0 (d, J = 9.8 Hz), 120.8 (d, J = 10.7 Hz), 119.3 (d, J = 24.1 Hz), 61.2. **HRMS** (ESI, *m/z*) calcd for $C_{32}H_{24}N_4F_4Br_4Cu$ (M^+): 918.7967, found: 918.7988. UV-VIS (3.2 mg/10mL CH_2Cl_2): λ_{max} = 412 nm (38).

General procedure of ATRA reaction using styrene derivatives and CBr_4

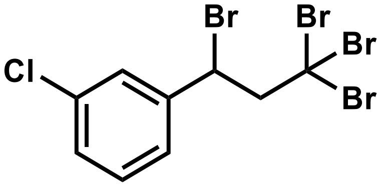
A septum-capped 20 mL reaction vial was charged with CBr_4 (**7**, 99.5 mg, 0.3 mmol), photocatalyst (**6**, 1 or 2.5 mol%) and a stirrer bar. The vial was sealed, then evacuated and back-filled with argon (3x). Dry, degassed DCM (1.5 mL) was added with a syringe followed by the styrene derivative (**8**, 0.3 mmol). Argon was bubbled through the solution for a couple of minutes. The cap of the vial was thoroughly wrapped around with parafilm. The vial was placed in the 6-pack reactor and was irradiated with green LEDs (520-525 nm) at 15-20°C. After 18 hours the solvent was removed by reduced pressure. Short column chromatography (using silica gel and *n*-hexane) afforded the products.



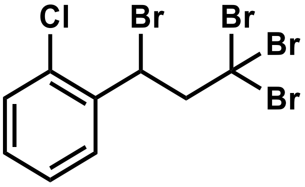
(1,3,3,3-Tetrabromopropyl)benzene (9a).[13] Yield: 122 mg (0.28 mmol, 93%), white solid, **MP:** 59-60 °C. R_f: 0.51 (hexanes). **IR** (ATR, cm^{-1}): 1644, 1489, 1452, 1417, 960, 727, 697. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.50 (d, J = 7.0 Hz, 2H), 7.36 (q, J = 7.7, 7.1 Hz, 3H), 5.34 (dd, J = 7.4, 4.4 Hz, 1H), 4.22 – 3.97 (m, 2H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 140.9, 129.1, 129.0, 128.3, 66.6, 50.19, 35.19.



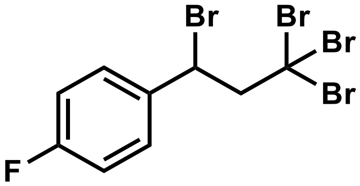
1-Chloro-4-(1,3,3,3-tetrabromopropyl)benzene (9b). Yield: 124 mg (0.26 mmol, 87%), white solid, **MP:** 77-78 °C. R_f: 0.39 (hexanes). **IR** (ATR, cm^{-1}): 1642, 1497, 1415, 1096, 1014, 964, 831. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.57 – 7.30 (m, 4H), 5.32 (dd, J = 8.1, 4.1 Hz, 1H), 4.23 – 3.72 (m, 2H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 139.3, 134.9, 129.7, 129.2, 66.4, 49.0, 34.8. **HRMS** (ESI, *m/z*) calcd for $C_9H_7ClBr_4$ (M^+): 465.6964, found: 465.6997.



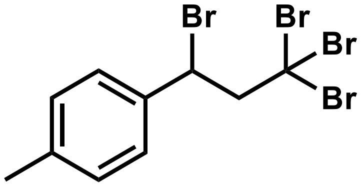
1-Chloro-3-(1,3,3,3-tetrabromopropyl)benzene (9c). Yield: 126 mg (0.27 mmol, 89%), colorless oil. R*f*: 0.34 (hexanes). **IR** (ATR, cm^{-1}): 1598, 1581, 1480, 1428, 1202, 1079, 975, 796, 738, 680. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.33 (dq, *J* = 11.9, 6.8, 5.7 Hz, 3H), 5.27 (dd, *J* = 7.8, 4.2 Hz, 1H), 4.18 – 3.91 (m, 2H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 142.7, 134.7, 130.3, 129.3, 128.5, 126.5, 66.3, 48.7, 34.7. **HRMS** (ESI, *m/z*) calcd for $C_9H_7ClBr_4$ (M^+): 465.6964, found: 465.6904.



1-Chloro-2-(1,3,3,3-tetrabromopropyl)benzene (9d). Yield: 128 mg (0.27 mmol, 91%), colorless oil. R*f*: 0.32 (hexanes). **IR** (ATR, cm^{-1}): 1644, 1478, 1445, 1420, 1200, 1161, 1132, 1038, 956, 748, 688. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.24 (m, 3H), 5.99 – 5.76 (m, 1H), 4.35 – 3.98 (m, 2H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 138.5, 133.2, 130.3, 130.1, 130.0, 127.7, 65.9, 45.1, 34.8. **HRMS** (ESI, *m/z*) calcd for $C_9H_7ClBr_4$ (M^+): 465.6964, found: 465.6925.



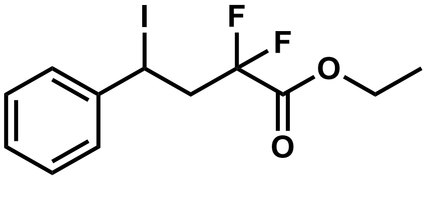
1-Fluoro-4-(1,3,3,3-tetrabromopropyl)benzene (9e). Yield: 124 mg (0.27 mmol, 91%), colorless oil. R*f*: 0.30 (hexanes). **IR** (ATR, cm^{-1}): 1611, 1502, 1420, 1221, 1159, 1098, 966, 833, 755, 710, 656. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.06 (t, *J* = 8.5 Hz, 2H), 5.34 (dd, *J* = 8.2, 4.0 Hz, 1H), 4.19 – 3.82 (m, 2H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 162.9 (d, *J* = 249.4 Hz), 136.7 (d, *J* = 3.3 Hz), 130.2 (d, *J* = 8.4 Hz), 116.0 (d, *J* = 21.8 Hz), 66.5, 49.3, 34.9. **HRMS** (ESI, *m/z*) calcd for $C_9H_7FBr_4$ (M^+): 449.7260, found: 449.7219.



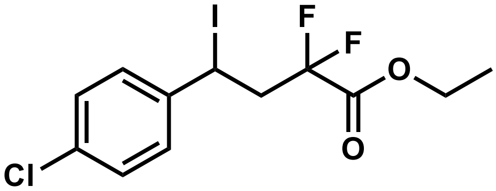
1-Methyl-4-(1,3,3,3-tetrabromopropyl)benzene (9f).[14] Yield: 74 mg (0.16 mmol, 54%), colorless oil. R*f*: 0.53 (hexanes). **IR** (ATR): 1650, 1514, 1420, 958, 820. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 5.34 (dd, *J* = 7.4, 4.5 Hz, 1H), 4.22 – 3.93 (m, 2H), 2.36 (s, 3H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 139.1, 138.0, 129.7, 128.2, 66.5, 50.4, 35.3, 21.4.

General procedure for ATRA reaction of styrene derivatives and ethyl iododifluoracetate

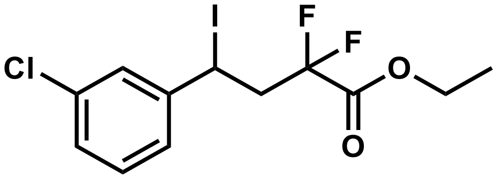
A septum-capped 20 mL reaction vial was charged with photocatalyst (5 or 10 mol%) and a stirrer bar. The vial was sealed, then evacuated and back-filled with argon (3x). Dry, degassed DCM (5 mL) was added with a syringe followed by the styrene derivative (**7**, 1.0 mmol) and ethyl iododifluoroacetate (**10**, 1.0 mmol). Argon was bubbled through the solution for a couple of minutes. The cap of the vial was thoroughly wrapped around with parafilm. The vial was placed in the 6-pack reactor and was irradiated with green LEDs (520-525 nm) at 15-20°C. The irradiation was stopped 3 or 6 hours. The reaction mixture was diluted with DCM (5 mL) and washed with water (3 x 5 mL). After that, the organic phase was dried, filtered and evaporated. Flash column chromatography (using silica gel, hexane and DCM as solvents) afforded the products.



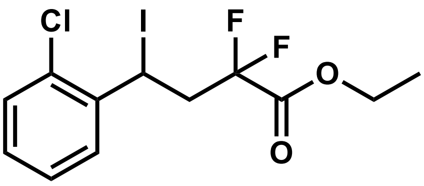
Ethyl 2,2-difluoro-4-iodo-4-phenylbutanoate (11a). Yield: 266 mg (0.75 mmol, 75%), pale yellow solid, **MP:** 48–50 °C. R*f*: 0.61 (hexane-DCM 1:1). **IR** (ATR, cm^{-1}): 1769, 1760, 1456, 1374, 1187, 1092, 1068, 766, 697. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.48 – 7.35 (m, 2H), 7.35 – 7.19 (m, 3H), 5.32 (dd, *J* = 9.6, 5.5 Hz, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.43 – 3.03 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 163.2 (t, *J* = 32.1 Hz), 142.5, 128.8, 128.6, 127.3, 114.3 (t, J = 255.0 Hz), 63.2, 46.5 (t, J = 23.9 Hz), 18.8 (dd, J = 6.4, 4.0 Hz), 13.9. **HRMS** (ESI, *m/z*) calcd for $C_{12}H_{13}F_2O_2$ (M-I): 227.0878, found: 227.0860.



Ethyl 4-(4-chlorophenyl)-2,2-difluoro-4-iodobutanoate (11b). Yield: 312 mg (0.80 mmol, 80%), pale yellow solid, **MP:** 52–54 °C. R*f*: 0.72 (hexane-DCM 1:1). **IR** (ATR, cm^{-1}): 1771, 1763, 1637, 1491, 1376, 1094, 1081, 1016, 831. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 5.31 (dd, J = 9.7, 5.5 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 3.43 – 2.97 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 163.1 (t, J = 32.0 Hz), 141.2, 134.2, 129.0, 128.6, 114.3 (t, J = 255.0 Hz), 63.3, 46.3 (t, J = 23.7 Hz), 18.3 – 16.6 (m), 13.9. **HRMS** (ESI, *m/z*) calcd for $C_{12}H_{12}ClF_2O_2$ (M-I): 261.0488, found: 261.0487.

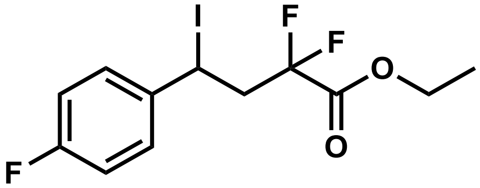


Ethyl 4-(3-chlorophenyl)-2,2-difluoro-4-iodobutanoate (11c). Yield: 324 mg (0.83 mmol, 83%), pale yellow solid, **MP:** 40–42 °C. R*f*: 0.65 (hexane-DCM 1:1). **IR** (ATR, cm^{-1}): 1762, 1594, 1571, 1476, 1434, 1217, 1189, 1077, 775, 693. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.22 (q, J = 5.4 Hz, 3H), 5.23 (dd, J = 9.6, 5.6 Hz, 1H), 4.07 (q, J = 7.2 Hz, 2H), 3.42 – 2.92 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 163.1 (t, J = 32.0 Hz), 144.5, 134.5, 130.1, 128.8, 127.5, 125.5, 114.2 (t, J = 253.5 Hz), 63.4, 46.2 (t, J = 23.8 Hz), 17.1 – 16.5 (m), 13.9. **HRMS** (ESI, *m/z*) calcd for $C_{12}H_{12}ClF_2O_2$ (M-I): 261.0488, found: 261.0473.

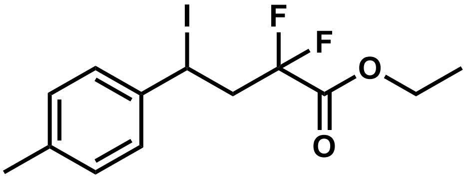


Ethyl 4-(2-chlorophenyl)-2,2-difluoro-4-iodobutanoate (11d). Yield: 312 mg (0.80 mmol, 80%), yellow oil. R*f*: 0.70 (hexane-DCM 1:1). **IR** (ATR, cm^{-1}): 1760, 1475, 1441, 1376, 1303, 1184, 1077, 1055, 1038, 852, 755. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.61 (d, J = 7.5 Hz, 1H), 7.41

– 7.13 (m, 3H), 5.86 (dd, *J* = 9.2, 5.9 Hz, 1H), 4.16 (qd, *J* = 7.2, 2.4 Hz, 2H), 3.49 – 3.13 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 163.1 (t, *J* = 32.0 Hz), 139.6, 131.9, 130.2, 129.5, 128.9, 127.5, 114.3 (t, *J* = 253.6 Hz), 63.3, 45.0 (t, *J* = 23.9 Hz), 13.8, 13.3 (t, *J* = 5.0 Hz). **HRMS** (ESI, *m/z*) calcd for $C_{12}H_{12}ClF_2IO_2$ (M^+): 387.9539, found: 387.9523.



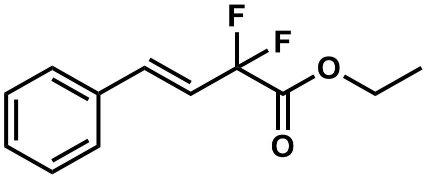
Ethyl 2,2-difluoro-4-(4-fluorophenyl)-4-iodobutanoate (11e). Yield: 310 mg (0.83 mmol, 83%), pale yellow solid, **MP:** 49–50 °C. R_f: 0.56 (hexane-DCM 1:1). **IR** (ATR, cm^{-1}): 1763, 1603, 1510, 1378, 1337, 1303, 1225, 1081, 839, 779. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.48 – 7.33 (m, 2H), 7.07 – 6.90 (m, 2H), 5.33 (dd, *J* = 9.7, 5.5 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.37 – 3.08 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 163.1 (t, *J* = 32.0 Hz), 162.3 (d, *J* = 248.7 Hz), 138.5 (d, *J* = 3.4 Hz), 129.1 (d, *J* = 8.4 Hz), 115.8 (d, *J* = 21.9 Hz), 114.2 (t, *J* = 253.8 Hz), 63.3, 46.6 (t, *J* = 23.7 Hz), 17.7 (dd, *J* = 6.1, 4.0 Hz), 13.9. **HRMS** (ESI, *m/z*) calcd for: $C_{12}H_{12}F_3O_2$ (M-I): 245.0784, found: 245.0777.



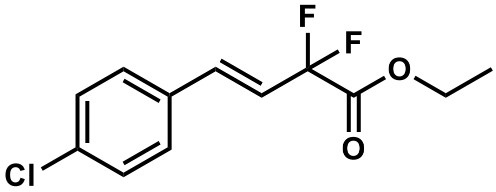
Ethyl 2,2-difluoro-4-iodo-4-(p-tolyl)butanoate (11f). Yield: 279 mg (0.75 mmol, 75%), pale yellow solid, **MP:** 43–45 °C. R_f: 0.55 (hexane-DCM 1:1). **IR** (ATR, cm^{-1}):1760, 1612, 1514, 1376, 1337, 1301, 1186, 1077, 820, 779, 720. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 5.35 (dd, *J* = 9.6, 5.5 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.45 – 3.05 (m, 2H), 2.31 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 163.2 (t, *J* = 32.0 Hz), 139.6, 138.6, 129.5, 127.1, 114.3 (t, *J* = 253.8 Hz), 63.1, 46.5 (t, *J* = 23.8 Hz), 21.3, 20.4 – 17.6 (m), 13.8. **HRMS** (ESI, *m/z*) calcd for: $C_{13}H_{15}F_2IO_2$ (M^+): 368.0085, found: 368.0080.

General procedure for preparation of the alkene derivatives

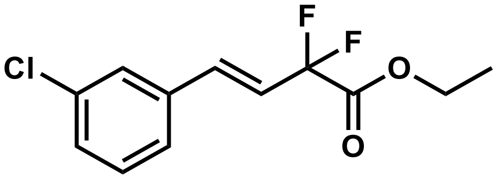
A septum-capped 20 mL reaction vial was charged with photocatalyst (5 or 10 mol%) and a stirrer bar. The vial was sealed, then evacuated and back-filled with argon (3x). Dry, degassed DCM (5 mL) was added with a syringe followed by the styrene derivative (**7**, 1.0 mmol) and ethyl iododifluoroacetate (**10**, 1.0 mmol). Argon was bubbled through the solution for a couple of minutes. The cap of the vial was thoroughly wrapped around with parafilm. The vial was placed in the 6-pack reactor and was irradiated with green LEDs (520-525 nm) at 15-20°C. The irradiation was stopped 3 or 6 hours. The reaction mixture was diluted with DCM (5 mL) and washed with 3 times with water (3 x 5 mL). After that, the organic phase was dried, filtered and trimethylamine (3.0 mmol, 3 equiv.) was added and the mixture was stirred at room temperature for 18 hours. After that, the mixture washed with water (2 x 5 mL). Then, the organic phase was dried, filtered and evaporated. Flash column chromatography (using silica gel, hexane and DCM as solvents) afforded the products.



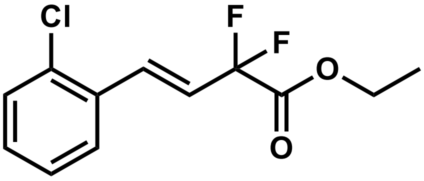
Ethyl (E)-2,2-difluoro-4-phenylbut-3-enoate (12a).[15] Yield: 179 mg (0.79 mmol, 79%), colorless oil. R*f*: 0.66 (hexane-DCM 1:1). **IR** (ATR, cm^{-1}): 1763, 1655, 1452, 1374, 1299, 1269, 1068, 971, 751. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 6.9, 3.0 Hz, 2H), 7.42 – 7.33 (m, 3H), 7.11 (dt, *J* = 16.2, 2.8 Hz, 1H), 6.34 (dt, *J* = 16.2, 11.4 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 164.0 (t, *J* = 34.9 Hz), 136.9 (t, *J* = 9.5 Hz), 134.2, 129.7, 128.9, 127.5, 119.0 (t, *J* = 25.0 Hz), 112.9 (t, *J* = 248.4 Hz), 63.2, 14.0.



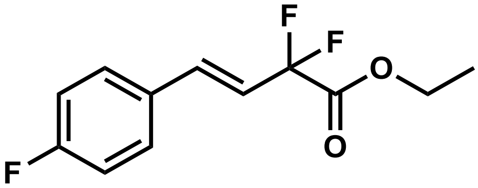
Ethyl (E)-4-(4-chlorophenyl)-2,2-difluorobut-3-enoate (12b).[15] Yield: 168 mg (0.64 mmol, 64%), colorless oil. R*f*: 0.62 (hexane-DCM 1:1). **IR** (ATR, cm^{-1}): 1767, 1659, 1493, 1409, 1372, 1286, 1195, 1076, 1014, 973. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.47 – 7.20 (m, 4H), 7.03 (dt, *J* = 16.2, 2.6 Hz, 1H), 6.29 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (63 MHz, CDCl$_3$) δ 163.8 (t, *J* = 34.8 Hz), 135.9 – 135.1 (m), 132.7, 129.1, 128.7, 119.6 (t, *J* = 25.1 Hz), 112.6 (t, *J* = 248.7 Hz), 63.3, 14.0.



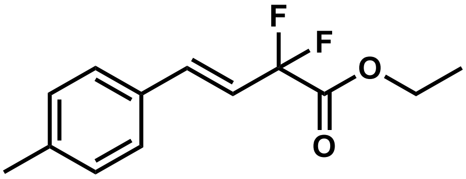
Ethyl (E)-4-(3-chlorophenyl)-2,2-difluorobut-3-enoate (12c).[15] Yield: 192 mg (0.73 mmol, 73%), colorless oil. R$_f$: 0.61 (hexane-DCM 1:1). **IR** (ATR, cm^{-1}): 1760, 1646, 1288, 1200, 1066, 969. **^{1}H NMR** (250 MHz, CDCl$_3$) δ 7.41 (d, *J* = 2.0 Hz, 1H), 7.30 (d, *J* = 1.5 Hz, 3H), 7.13 – 6.90 (m, 1H), 6.32 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (63 MHz, CDCl$_3$) δ 163.7 (t, *J* = 34.6 Hz), 136.0, 135.5 (t, *J* = 9.5 Hz), 134.9, 130.2, 129.6, 127.3, 125.8, 120.4 (t, *J* = 25.1 Hz), 112.5 (t, *J* = 248.9 Hz), 63.3, 14.0.



Ethyl (E)-4-(2-chlorophenyl)-2,2-difluorobut-3-enoate (12d).[15] Yield: 182 mg (0.70 mmol, 70%), colorless oil. R$_f$: 0.58 (hexane-DCM 1:1). **IR** (ATR, cm^{-1}): 1765, 1652, 1475, 1447, 1372, 1074, 969. **^{1}H NMR** (250 MHz, CDCl$_3$) δ 7.62 – 7.47 (m, 2H), 7.46 – 7.38 (m, 1H), 7.35 – 7.25 (m, 2H), 6.34 (dt, *J* = 16.1, 11.1 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (63 MHz, CDCl$_3$) δ 163.8 (t, *J* = 34.5 Hz), 134.4, 133.3 (t, *J* = 9.7 Hz), 132.5, 130.7, 130.1, 127.5, 127.2, 121.7 (t, *J* = 25.2 Hz), 112.6 (t, *J* = 248.7 Hz), 63.3, 14.1.



Ethyl (E)-2,2-difluoro-4-(4-fluorophenyl)but-3-enoate (12e).[15] Yield: 175 mg (0.71 mmol, 71%), colorless oil. R$_f$: 0.60 (hexane-DCM 1:1). **IR** (ATR, cm^{-1}): 1765, 1657, 1603, 1512, 1374, 1299, 1223, 1068, 971, 852, 820, 772. **^{1}H NMR** (250 MHz, CDCl$_3$) δ 7.47 – 7.35 (m, 2H), 7.06 (dt, *J* = 6.9, 2.1 Hz, 2H), 7.01 (q, *J* = 2.4 Hz, 1H), 6.23 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (63 MHz, CDCl$_3$) δ 163.9 (t, *J* = 34.8 Hz), 163.6 (d, *J* = 250.0 Hz), 135.7 (t, *J* = 9.5 Hz), 130.4 (d, *J* = 3.5 Hz), 129.4 (d, *J* = 8.3 Hz), 118.7 (td, *J* = 25.0, 2.4 Hz), 116.0 (d, *J* = 21.9 Hz), 112.8 (t, *J* = 248.5 Hz), 63.2, 14.0.



Ethyl (E)-2,2-difluoro-4-(p-tolyl)but-3-enoate (12f).[15] Yield: 178 mg (0.74 mmol, 74%), yellow oil. R*f*: 0.50 (hexane-DCM 1:1). **IR** (ATR, cm^{-1}): 1765, 1652, 1516, 1374, 1296, 1269, 1199, 1184, 1068, 973, 805, 720. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.07 (dt, *J* = 16.2, 2.6 Hz, 1H), 6.28 (dt, *J* = 16.2, 11.5 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 164.1 (t, *J* = 35.1 Hz), 139.9, 136.8 (t, *J* = 9.5 Hz), 131.4, 129.6, 127.5, 117.8 (t, *J* = 25.0 Hz), 113.0 (t, *J* = 248.3 Hz), 63.1, 21.4, 14.0.

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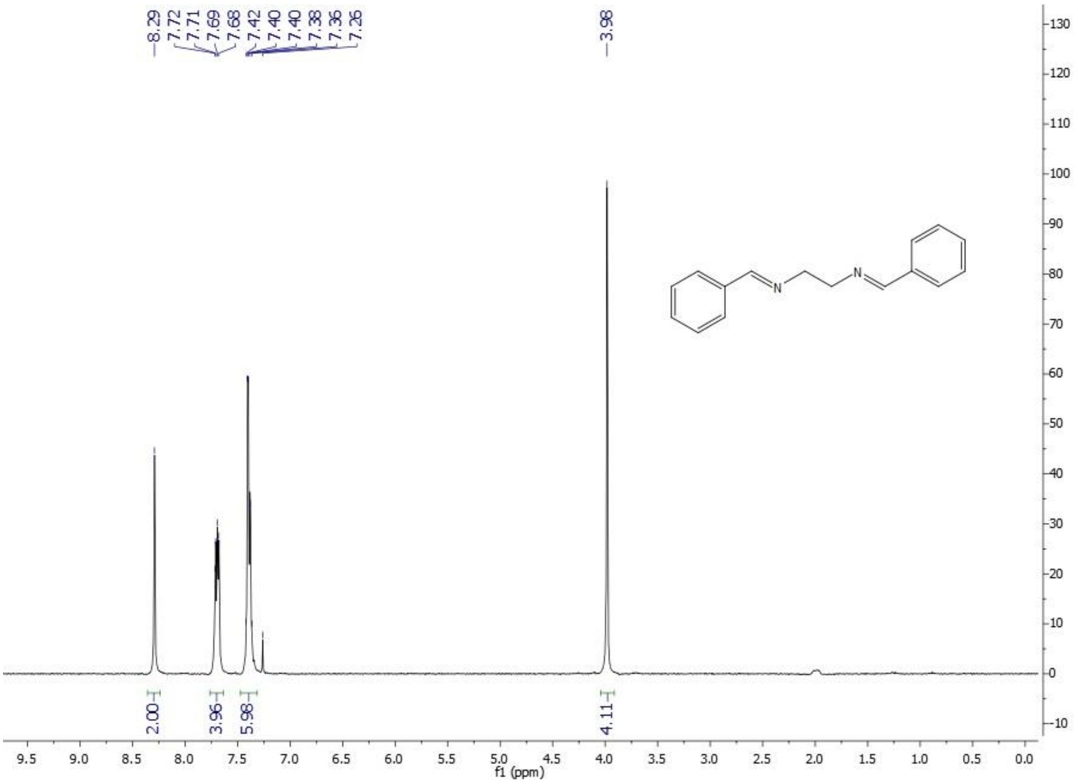
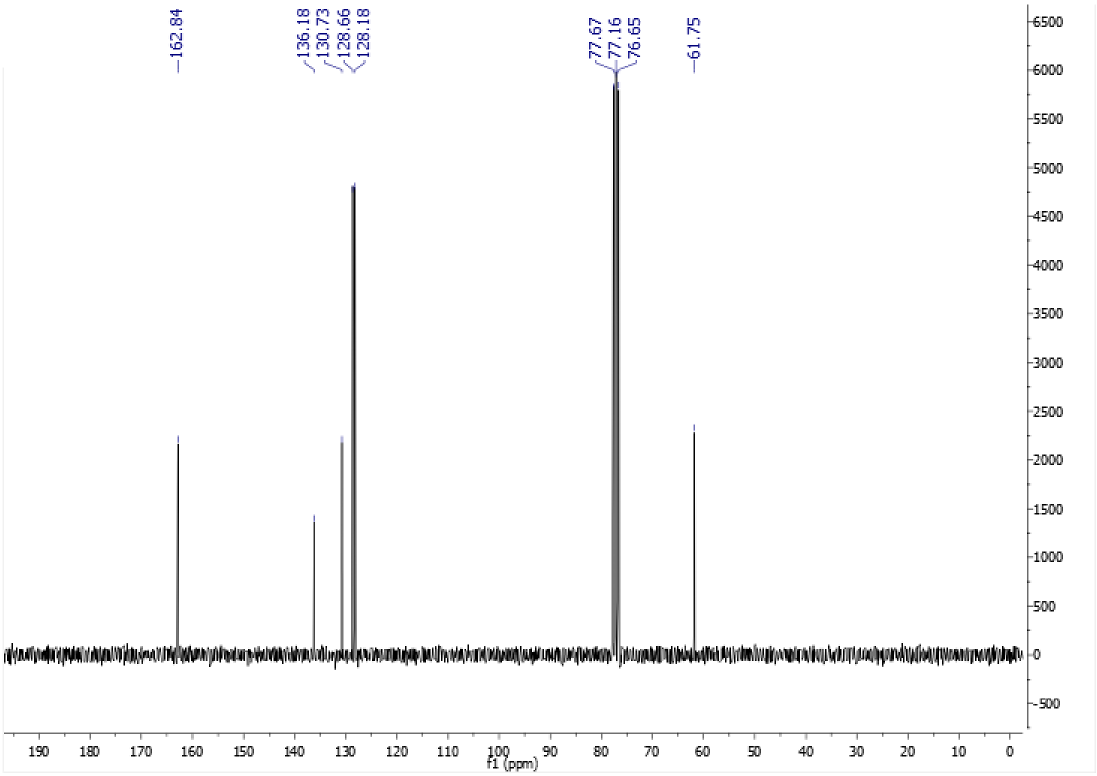
NMR spectra of the products

Compound **2a**





Compound **2b**

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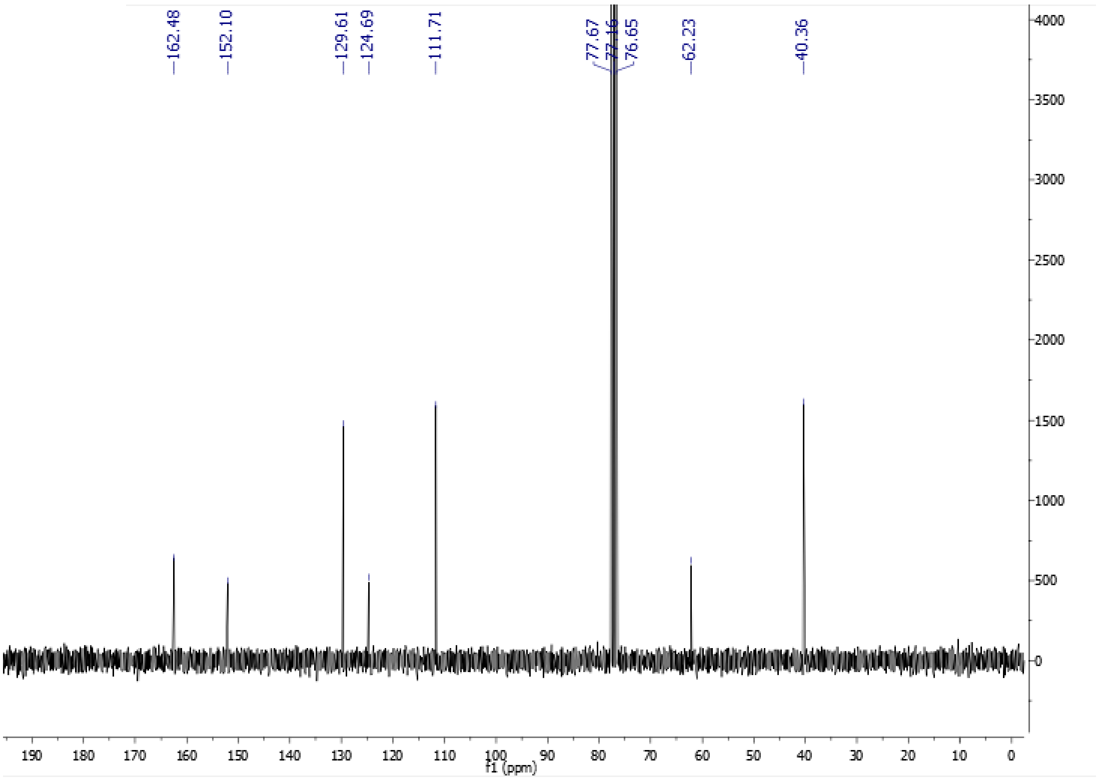
7.59
7.58
7.56
7.56
7.26
6.69
6.68
6.66
6.65
3.87
3.01
3.00
CH3
N
CH3
N
N
H3C
N
CH3
2.00
3.94
4.07
3.94
12.13
f1 (ppm)



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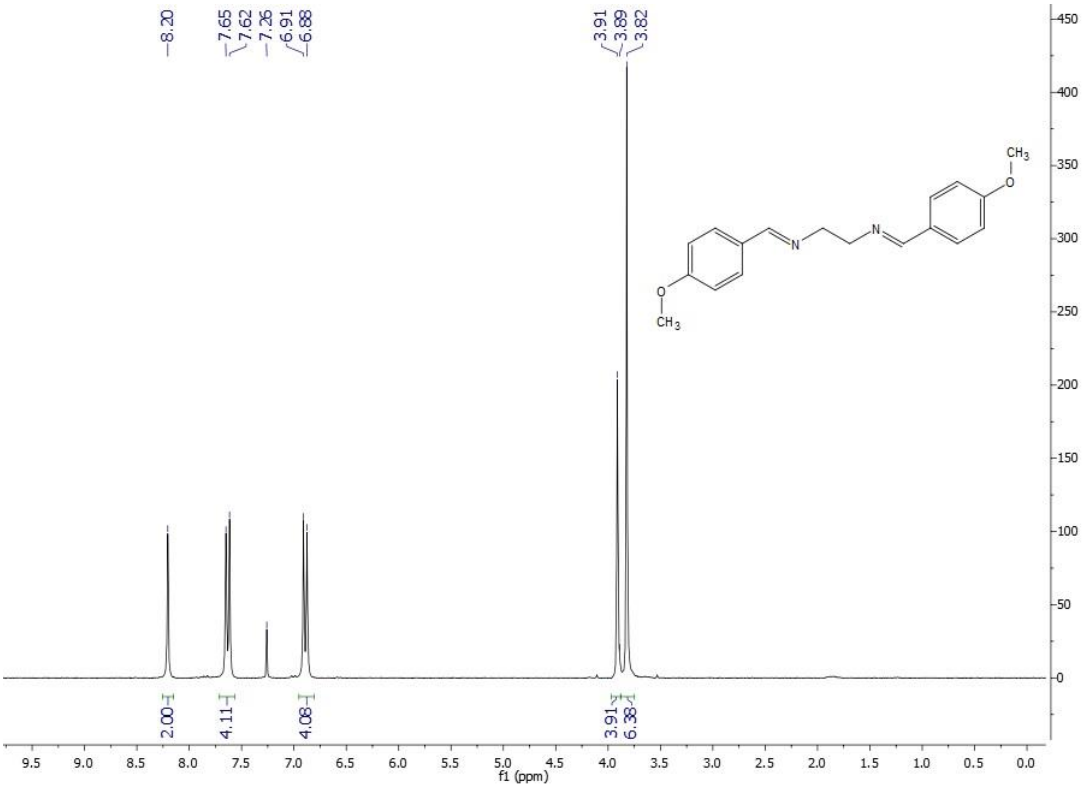
111.71
77.67
77.16
76.65
62.23
40.36
f1 (ppm)

Compound **2c**



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7.65
7.62
7.26
6.91
6.88
3.91
3.89
3.82
CH3
O
N
N
O
CH3
2.00
4.11
4.08
3.91
6.38
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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0.5
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f1 (ppm)
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200
150
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50
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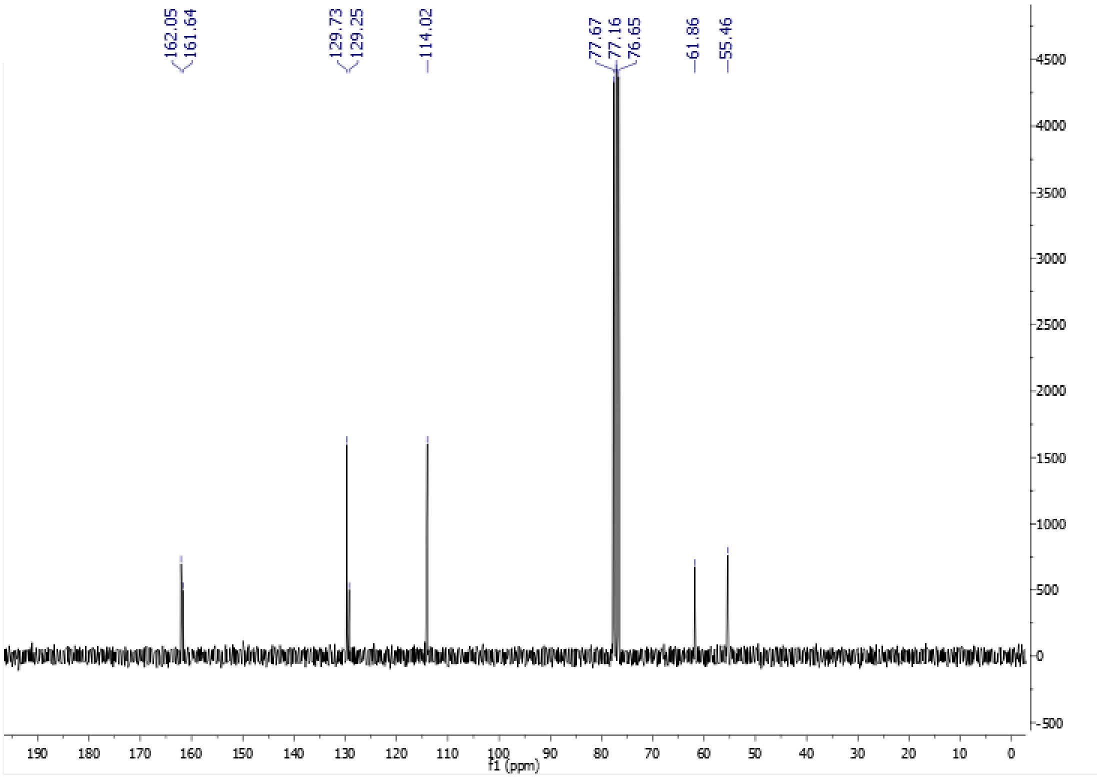

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76.65
61.86
55.46
190
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160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
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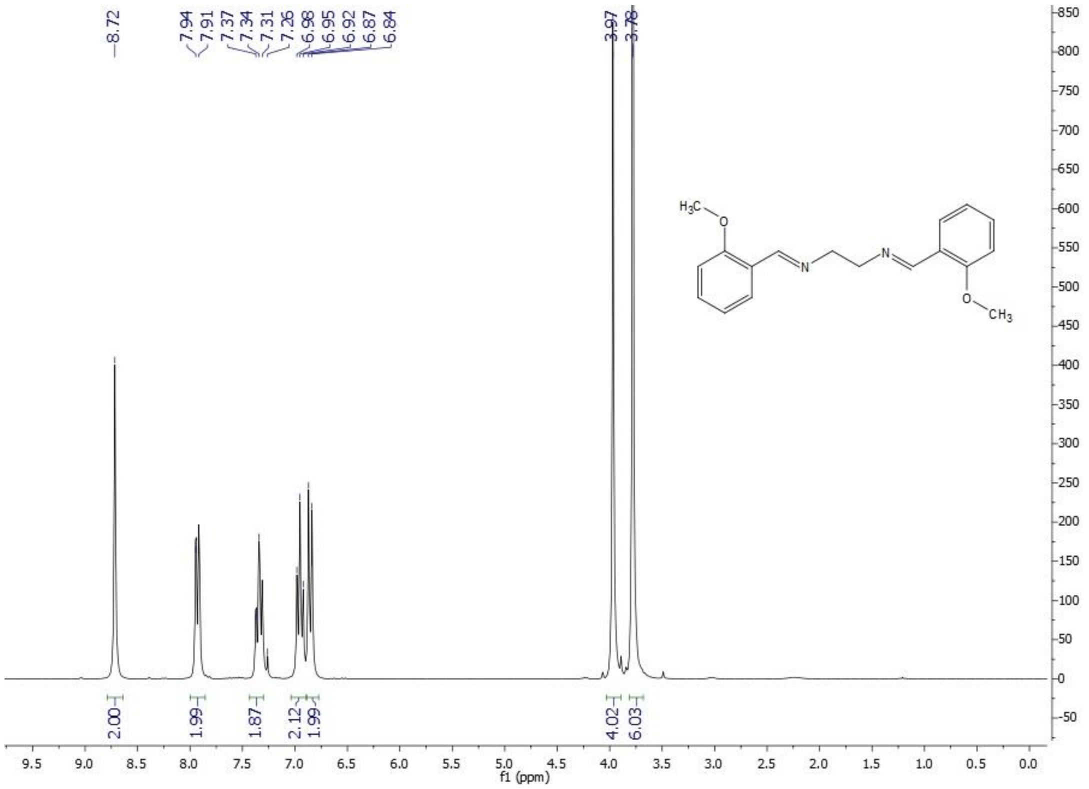
3500
3000
2500
2000
1500
1000
500
0
-500

Compound **2d**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6.92
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1.87
2.12
1.99
4.02
6.03
H3C
O
N
N
O
CH3
f1 (ppm)
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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
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100
50
0
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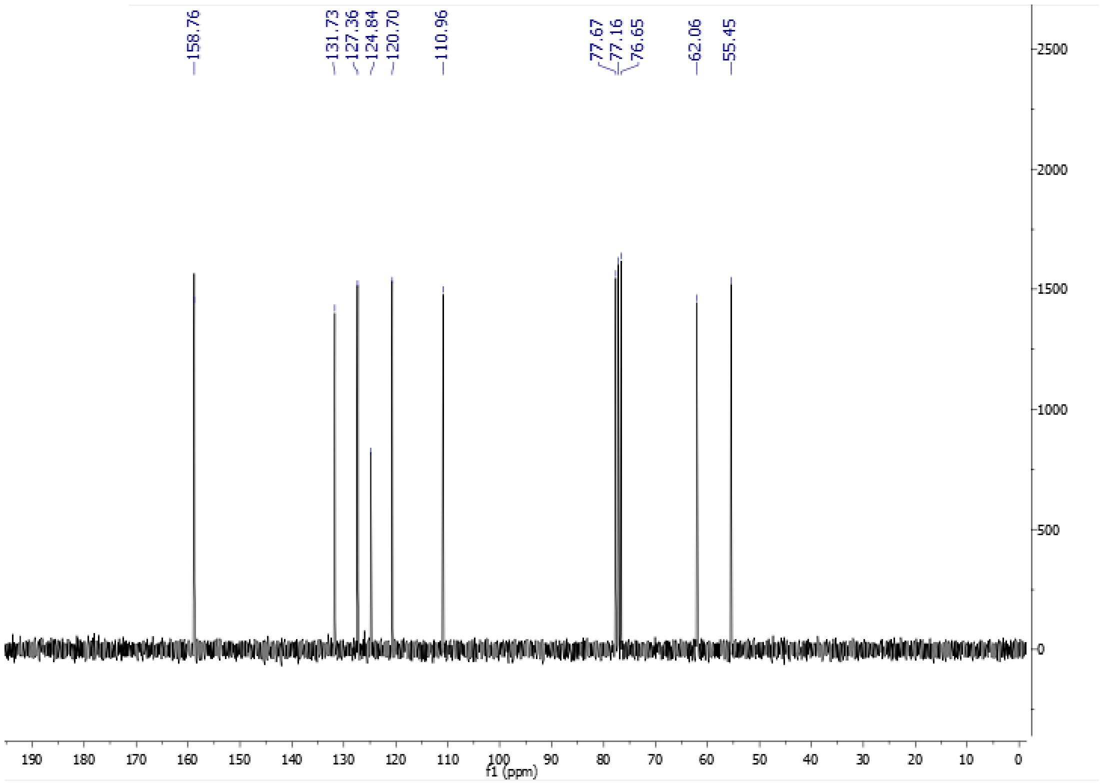
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77.67
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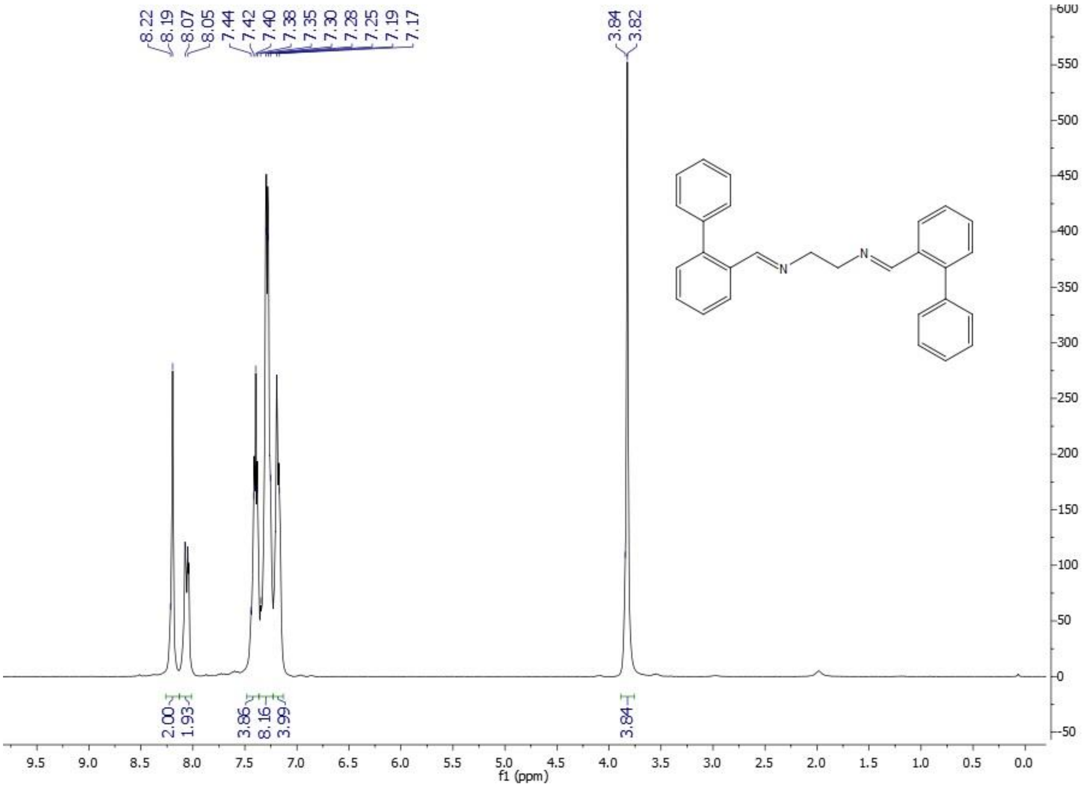
76.65
62.06
55.45
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
2500
2000
1500
1000
500
0

Compound **2e**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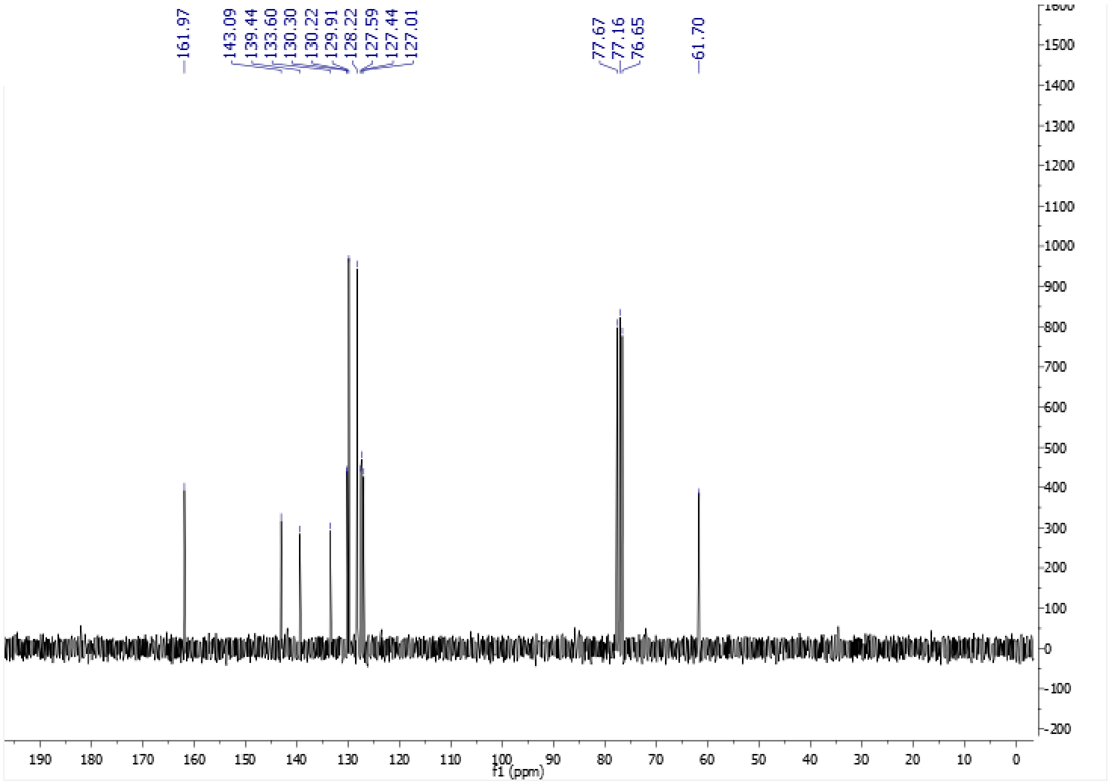
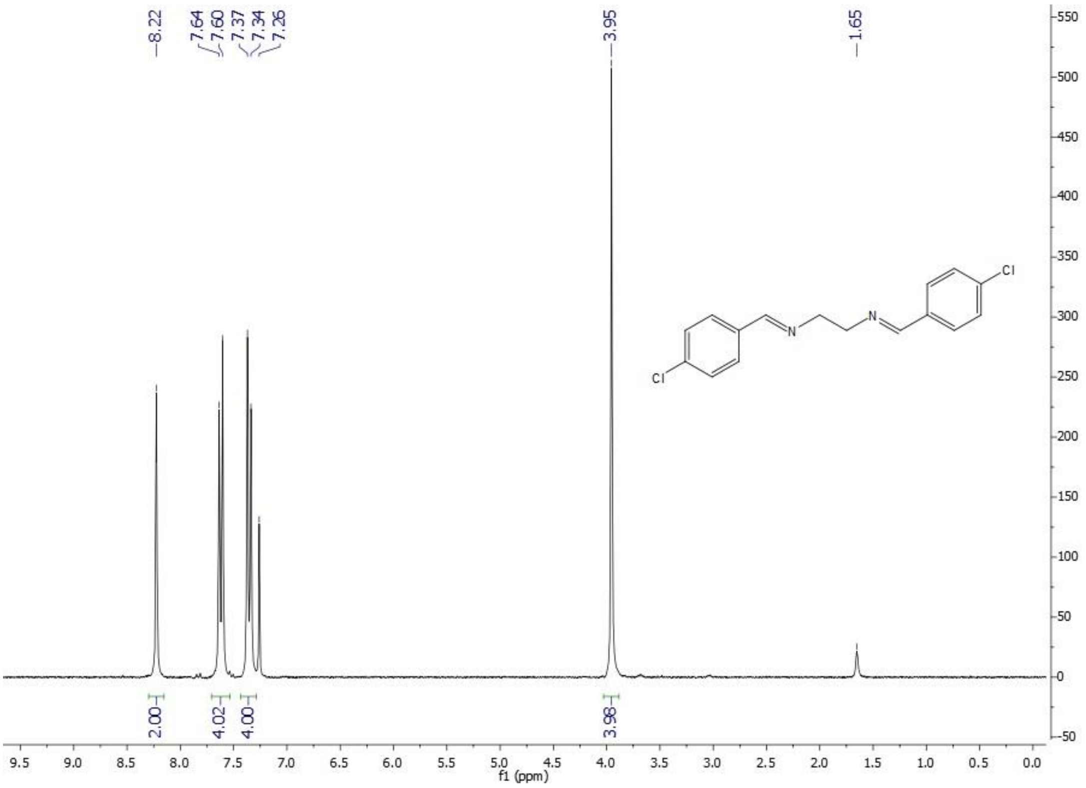
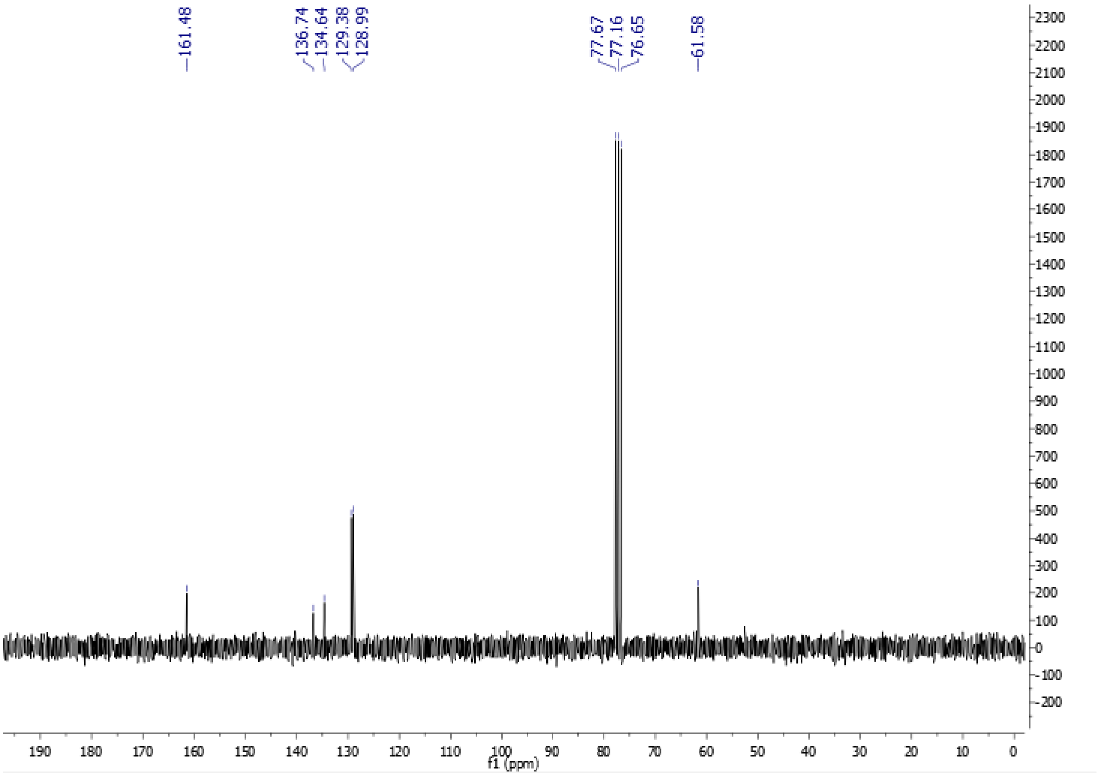
7.19
7.17
3.84
3.82
N
N
2.00
1.93
3.86
8.16
3.99
3.84
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
600 550 500 450 400 350 300 250 200 150 100 50 0 -50

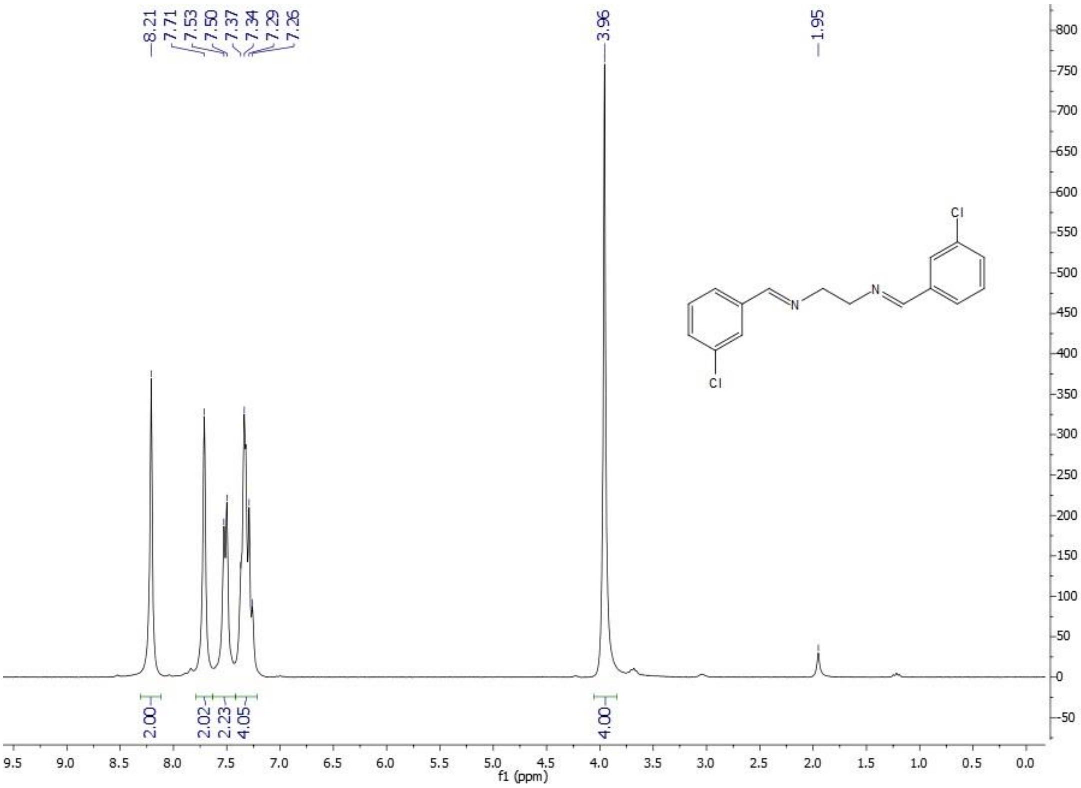

161.97
143.09
139.44
133.60
130.30
130.22
129.91
128.22
127.59
127.44
127.01
77.67
77.16
76.65
61.70
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200

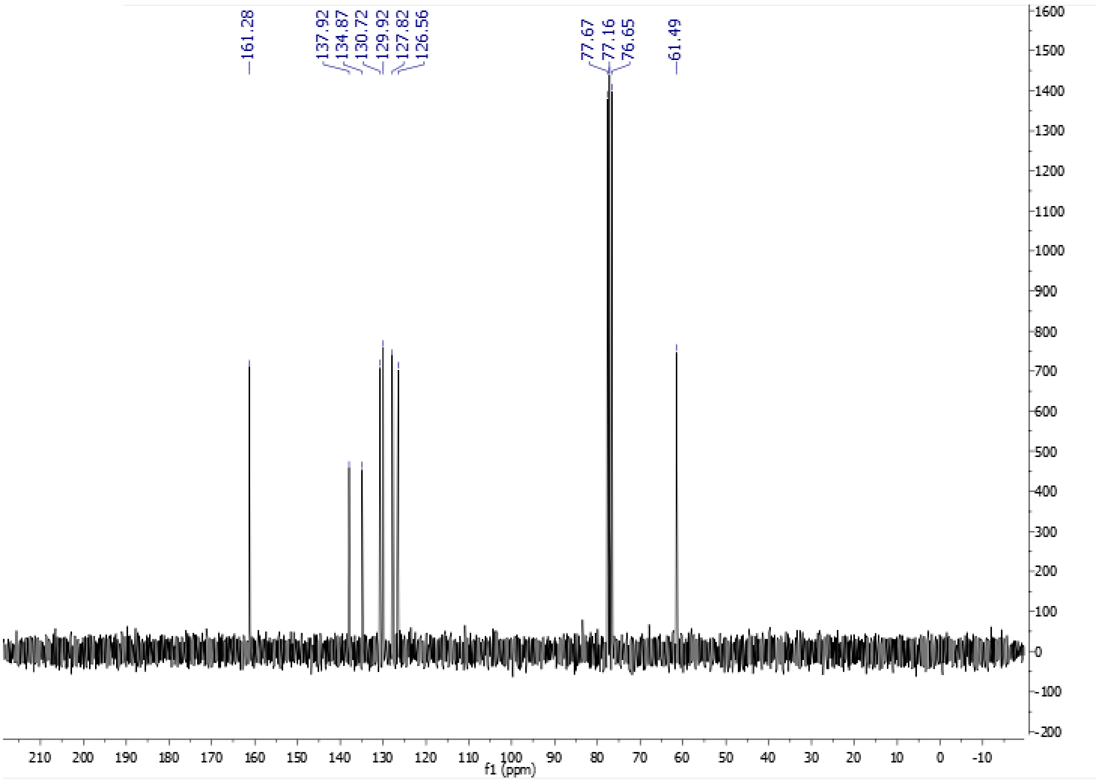
Compound **2f**


8.22
7.64
7.60
7.37
7.34
7.26
3.95
1.65
2.00
4.02
4.00
3.98
Cl
N
N
Cl
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
f1 (ppm)
550
500
450
400
350
300
250
200
150
100
50
0
-50

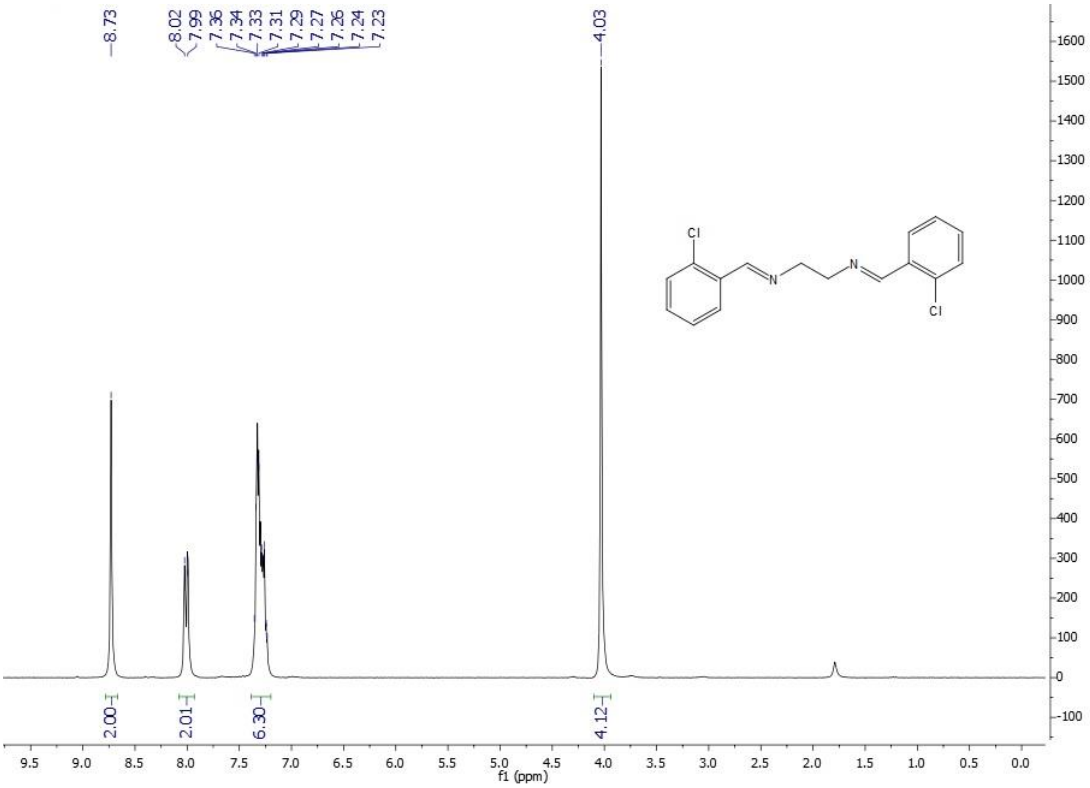

161.48
136.74
134.64
129.38
128.99
77.67
77.16
76.65
61.58
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200

Compound **2g**

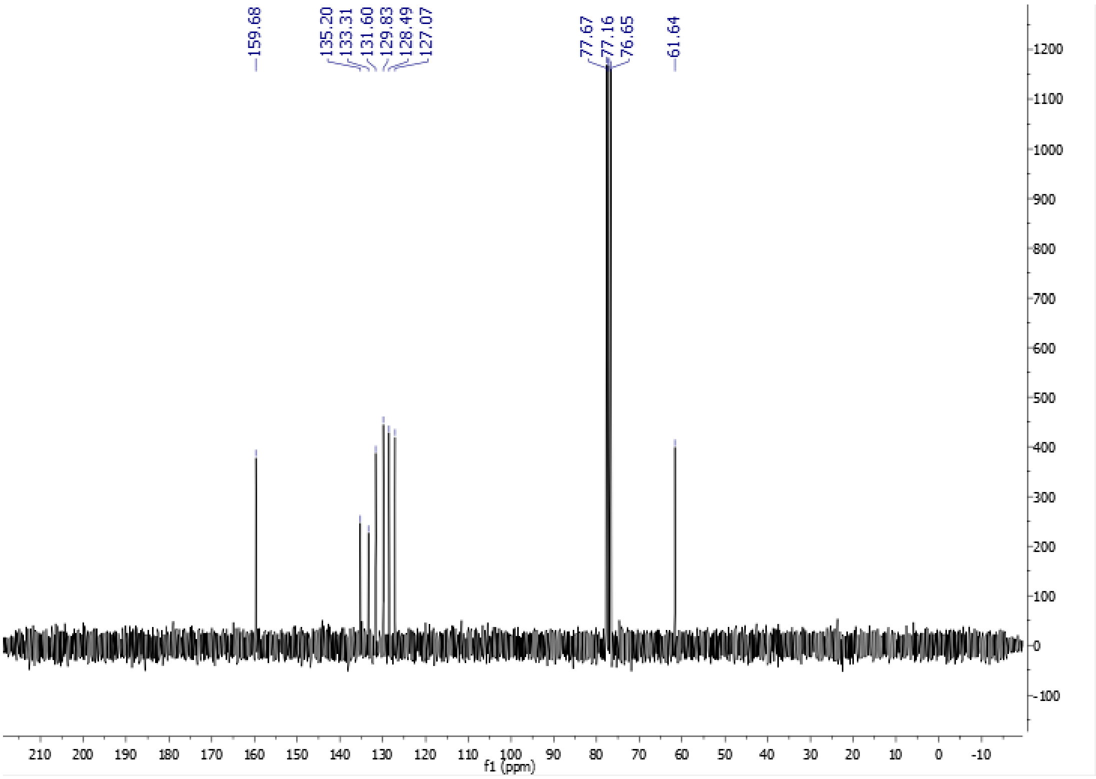

8.21
7.71
7.53
7.50
7.37
7.34
7.29
7.26
3.96
1.95
2.00
2.02
2.23
4.05
4.00
Cl
N
N
Cl
f1 (ppm)


161.28
137.92
134.87
130.72
129.92
127.82
126.56
77.67
77.16
76.65
61.49
f1 (ppm)

Compound **2h**

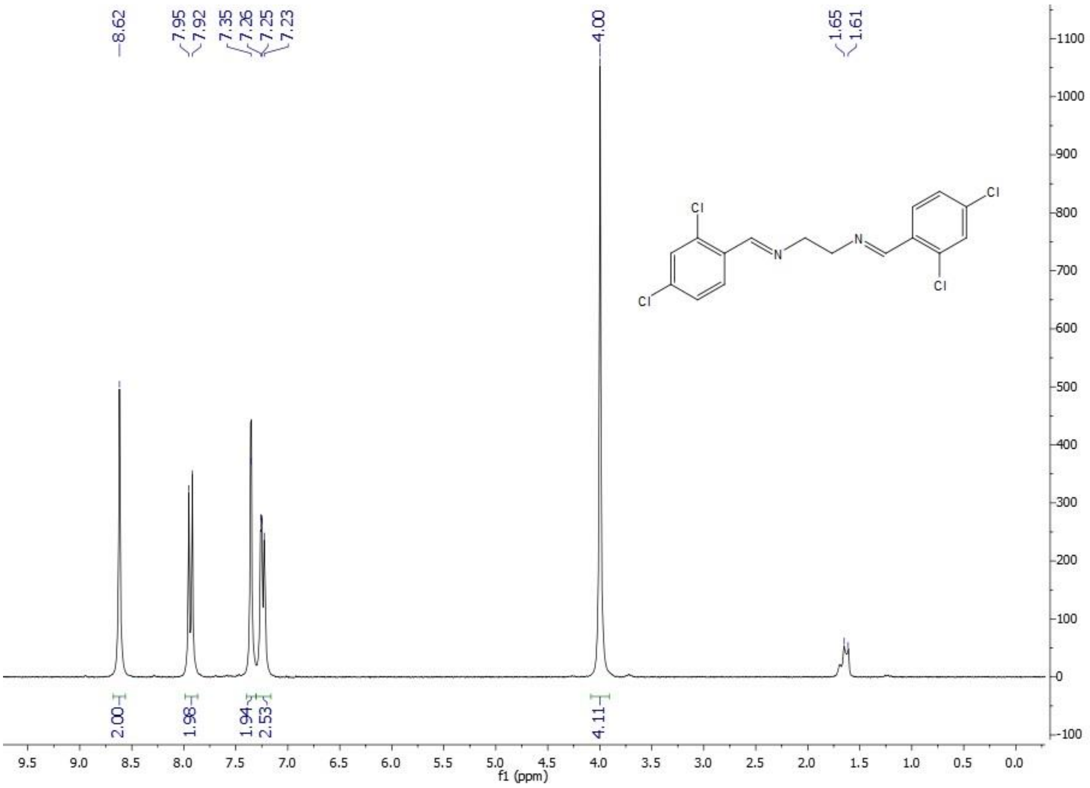


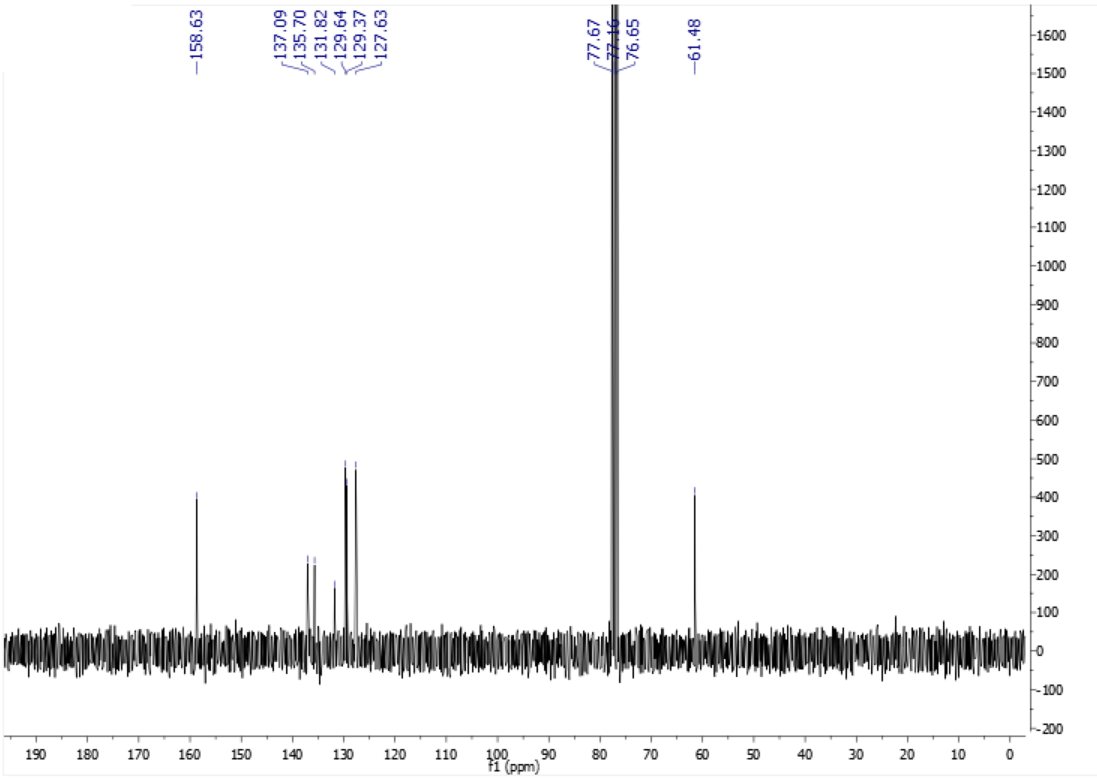
8.73
8.02
7.99
7.36
7.34
7.33
7.31
7.29
7.27
7.26
7.24
7.23
4.03
Cl
N
N
Cl
2.00
2.01
6.30
4.12
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



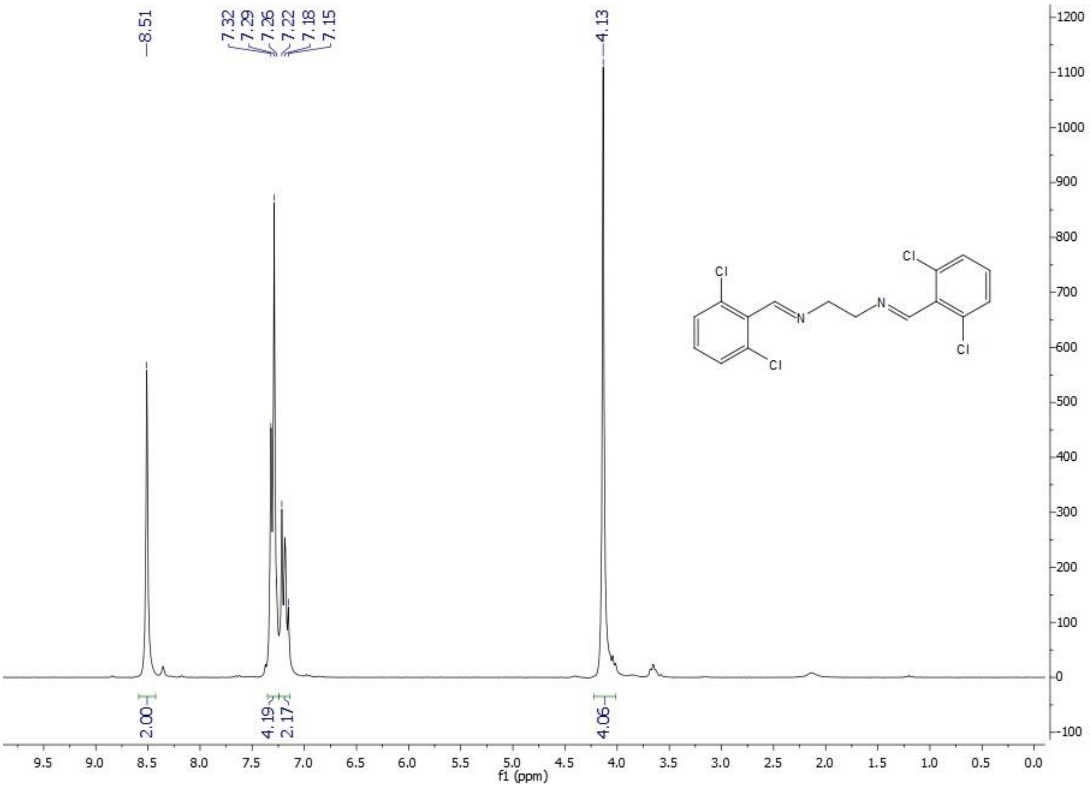
159.68
135.20
133.31
131.60
129.83
128.49
127.07
77.67
77.16
76.65
61.64
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

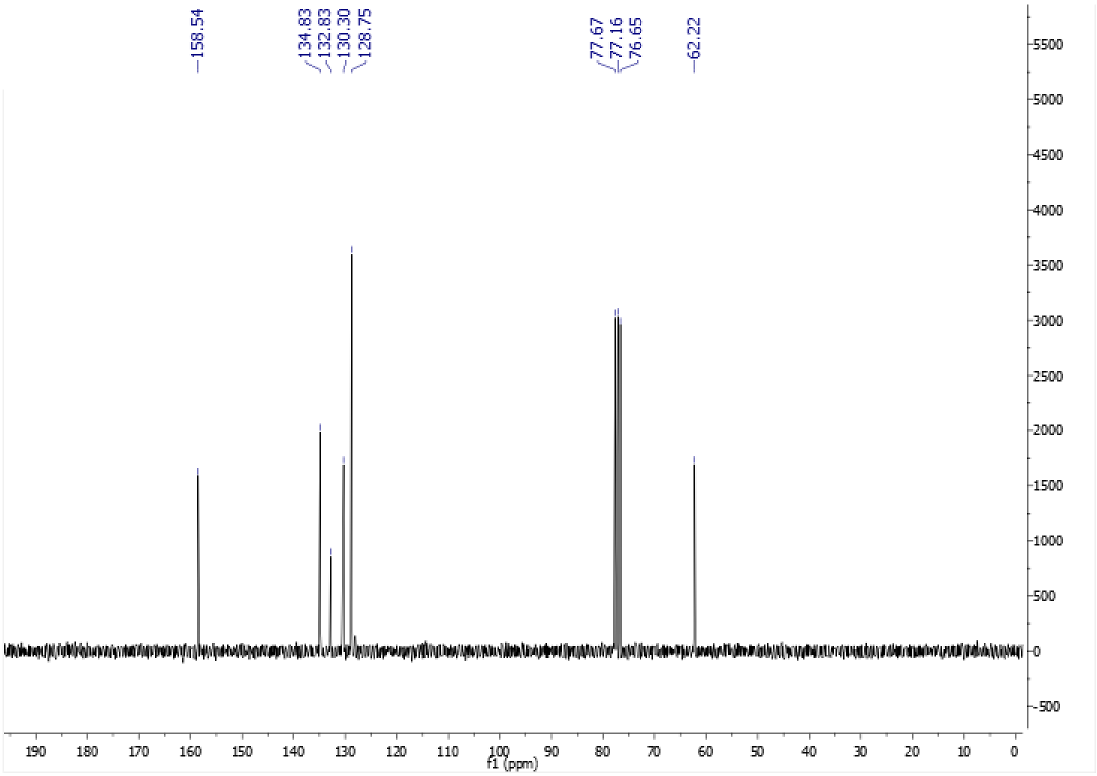
Compound **2i**


8.62
7.95
7.92
7.35
7.26
7.25
7.23
4.00
1.65
1.61
Cl
Cl
N
N
Cl
Cl
2.00
1.98
1.94
2.53
4.11
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
f1 (ppm)
1100 1000 900 800 700 600 500 400 300 200 100 0 -100

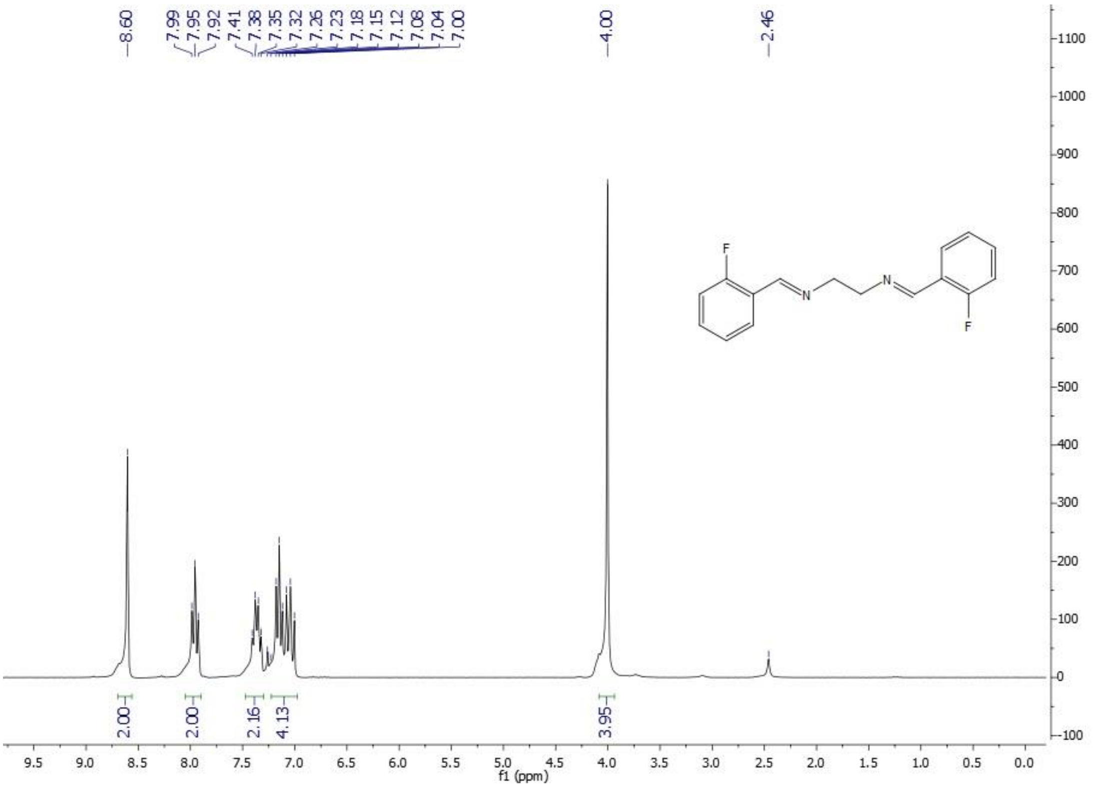

158.63
137.09
135.70
131.82
129.64
129.37
127.63
77.67
77.16
76.65
61.48
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200

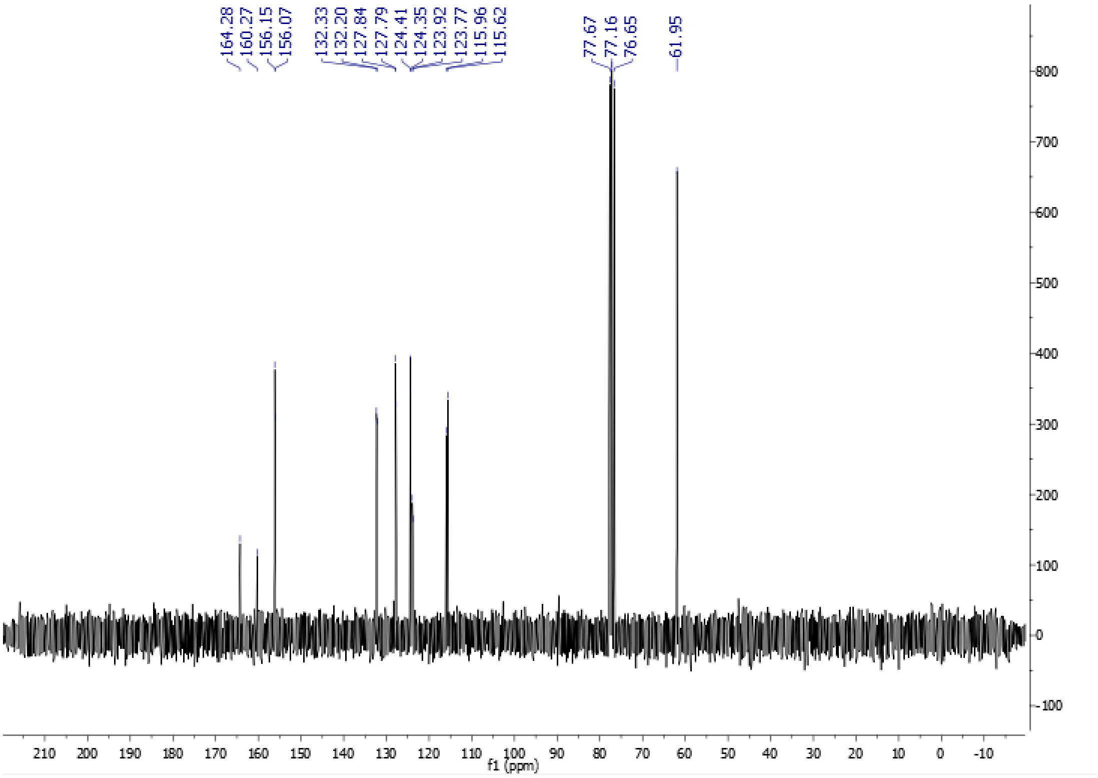
Compound **2j**


8.51
7.32
7.29
7.26
7.22
7.18
7.15
4.13
2.00
4.19
2.17
4.06
Cl
Cl
N
N
Cl
Cl
f1 (ppm)
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
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

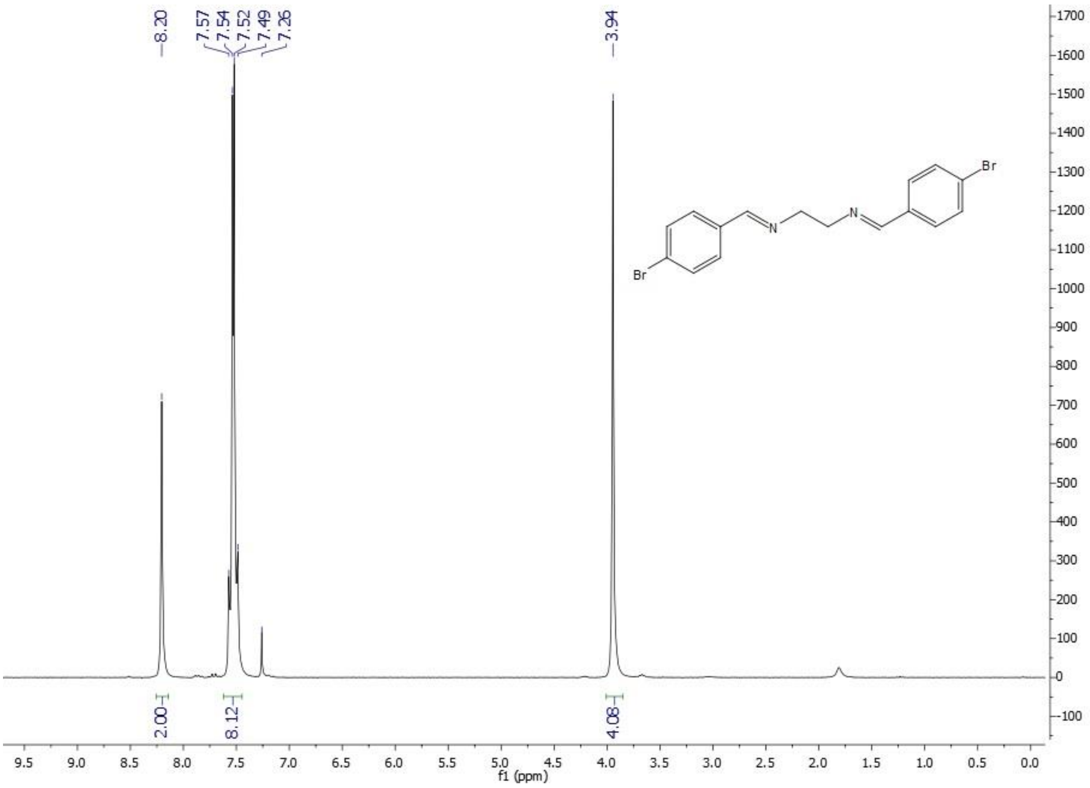

158.54
134.83
132.83
130.30
128.75
77.67
77.16
76.65
62.22
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

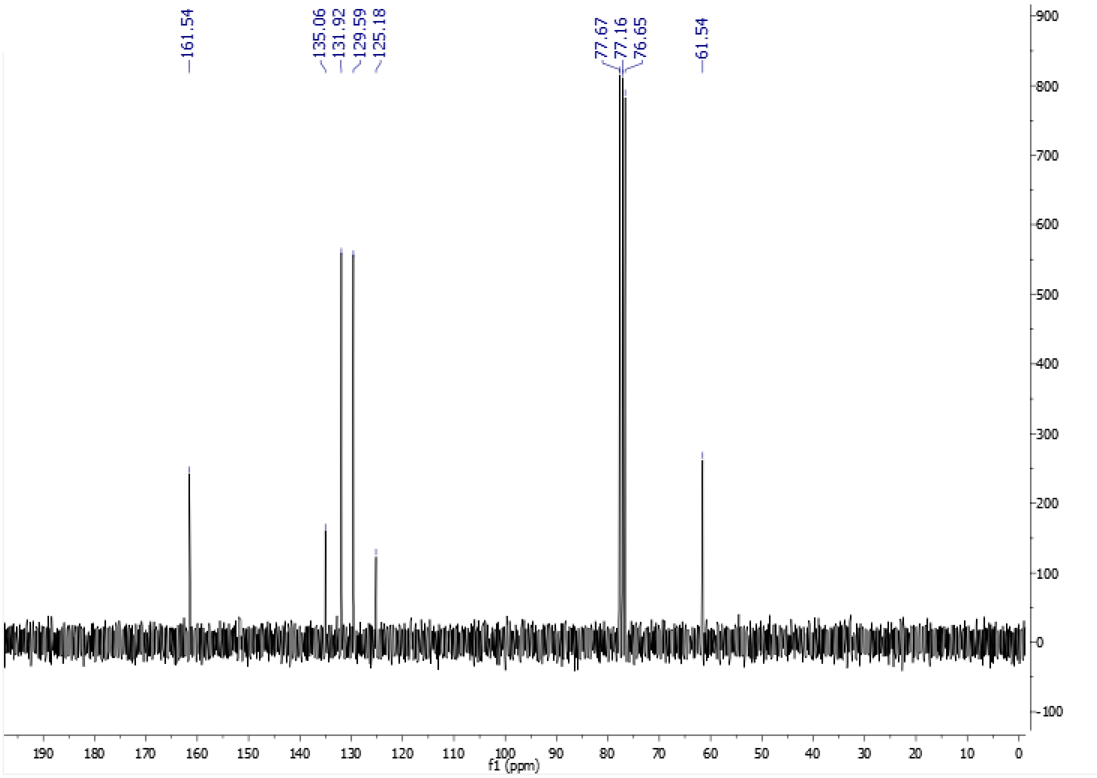
Compound **2k**


8.60
7.99
7.95
7.92
7.41
7.38
7.35
7.32
7.26
7.23
7.18
7.15
7.12
7.08
7.04
7.00
4.00
2.46
2.00
2.00
2.16
4.13
3.95
F
N
N
F
f1 (ppm)
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
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

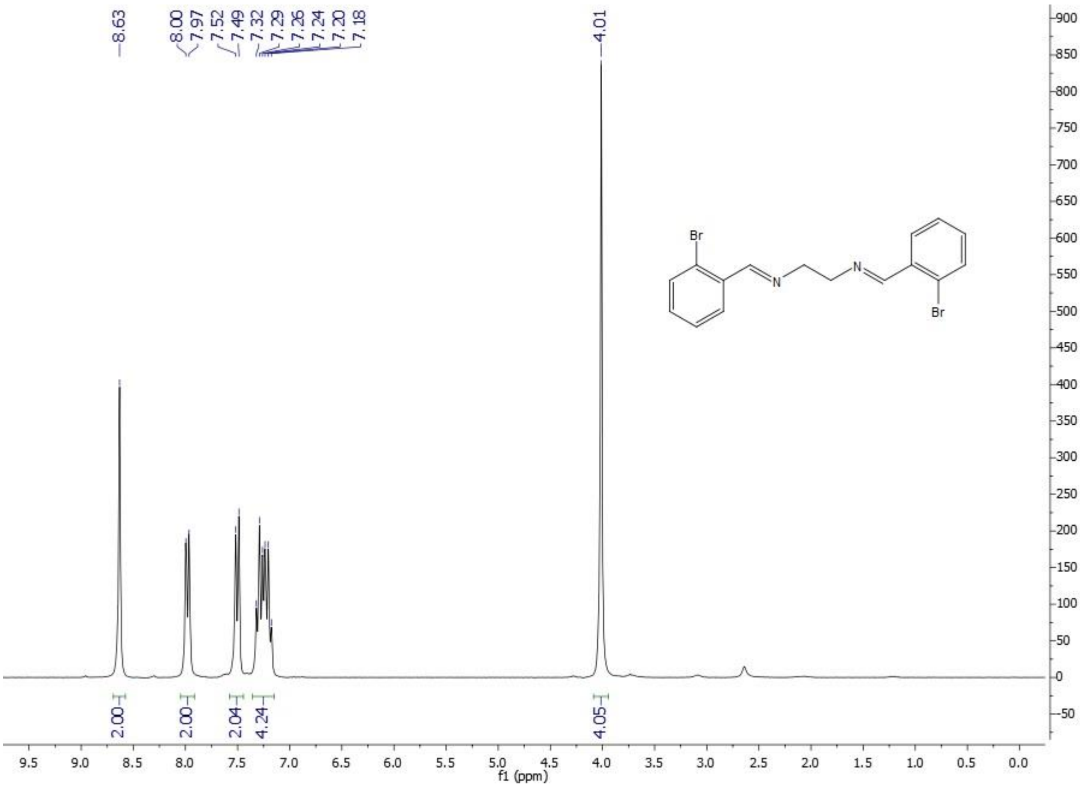

164.28
160.27
156.15
156.07
132.33
132.20
127.84
127.79
124.41
124.35
123.92
123.77
115.96
115.62
77.67
77.16
76.65
61.95
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
800
700
600
500
400
300
200
100
0
-100

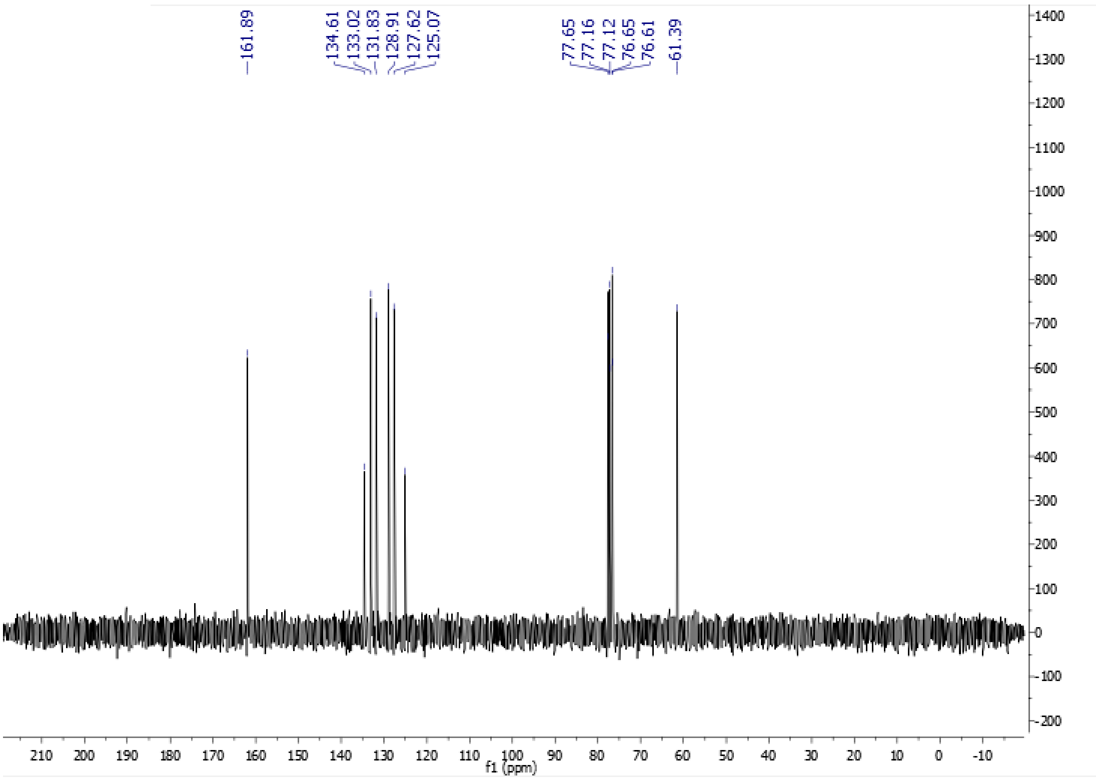
Compound **2l**


8.20
7.57
7.54
7.52
7.49
7.26
3.94
2.00
8.12
4.08
Br
N
N
Br
f1 (ppm)
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
1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

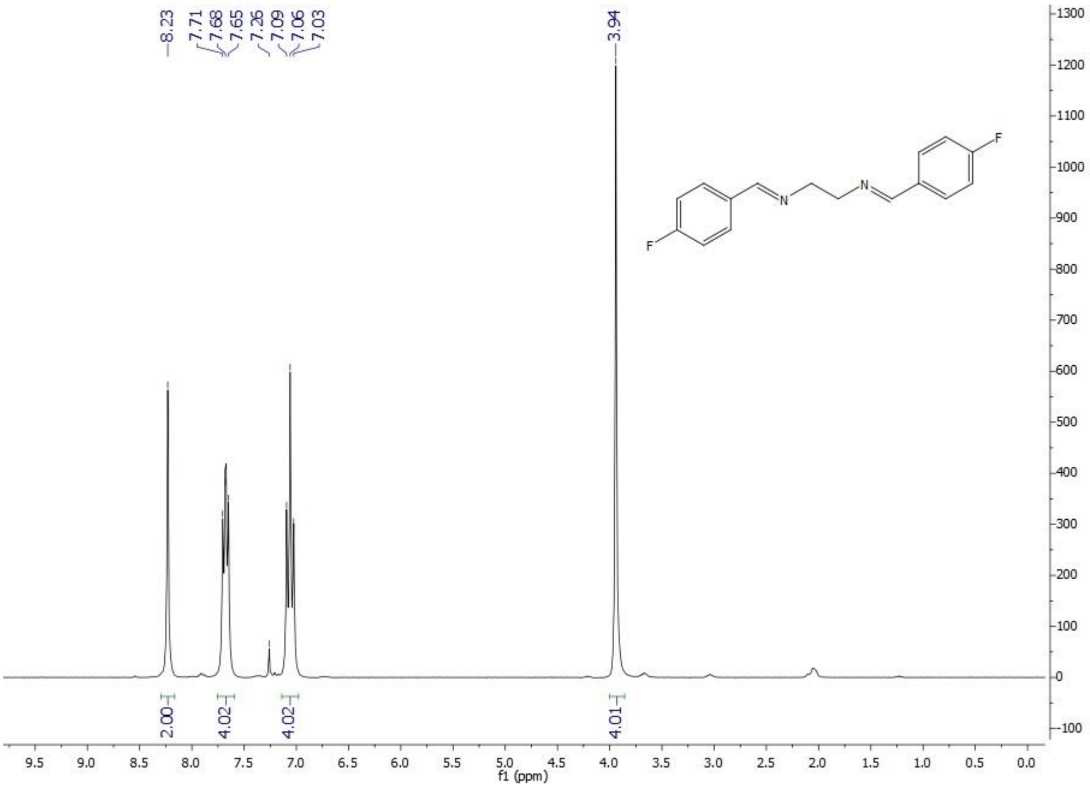

161.54
135.06
131.92
129.59
125.18
77.67
77.16
76.65
61.54
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
900 800 700 600 500 400 300 200 100 0 -100

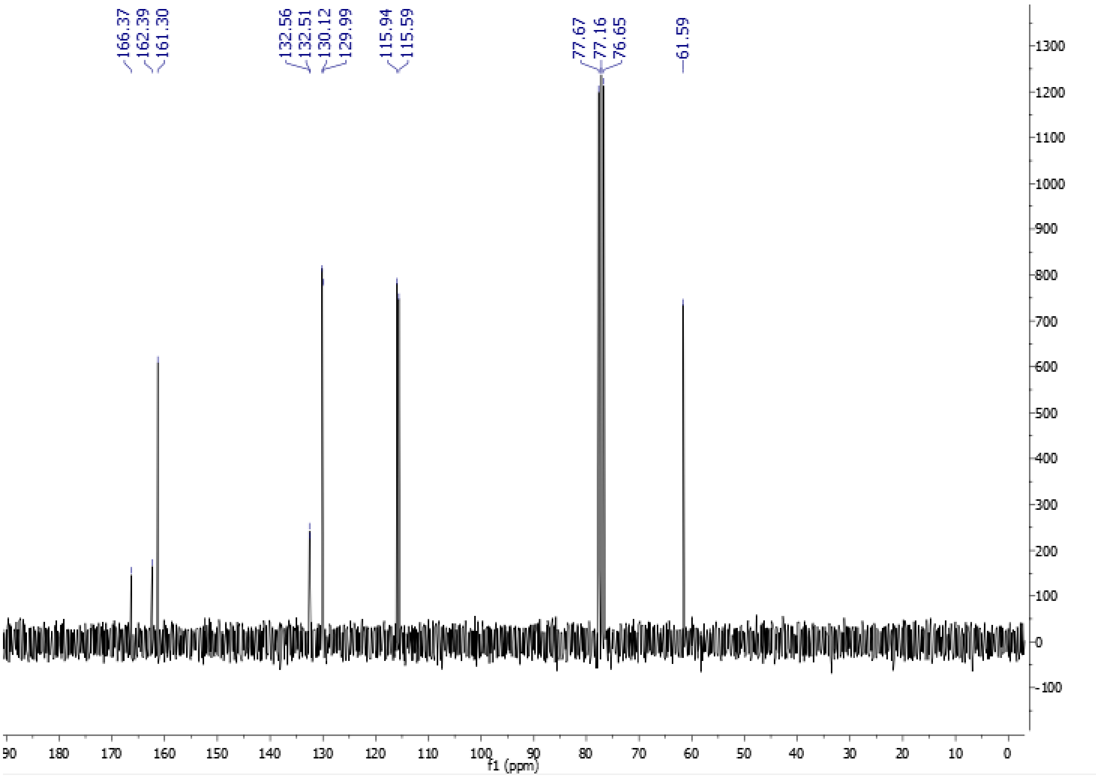
Compound **2m**


8.63
8.00
7.97
7.52
7.49
7.32
7.29
7.26
7.24
7.20
7.18
4.01
2.00
2.00
2.04
4.24
4.05
Br
N
N
Br
f1 (ppm)
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
900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50

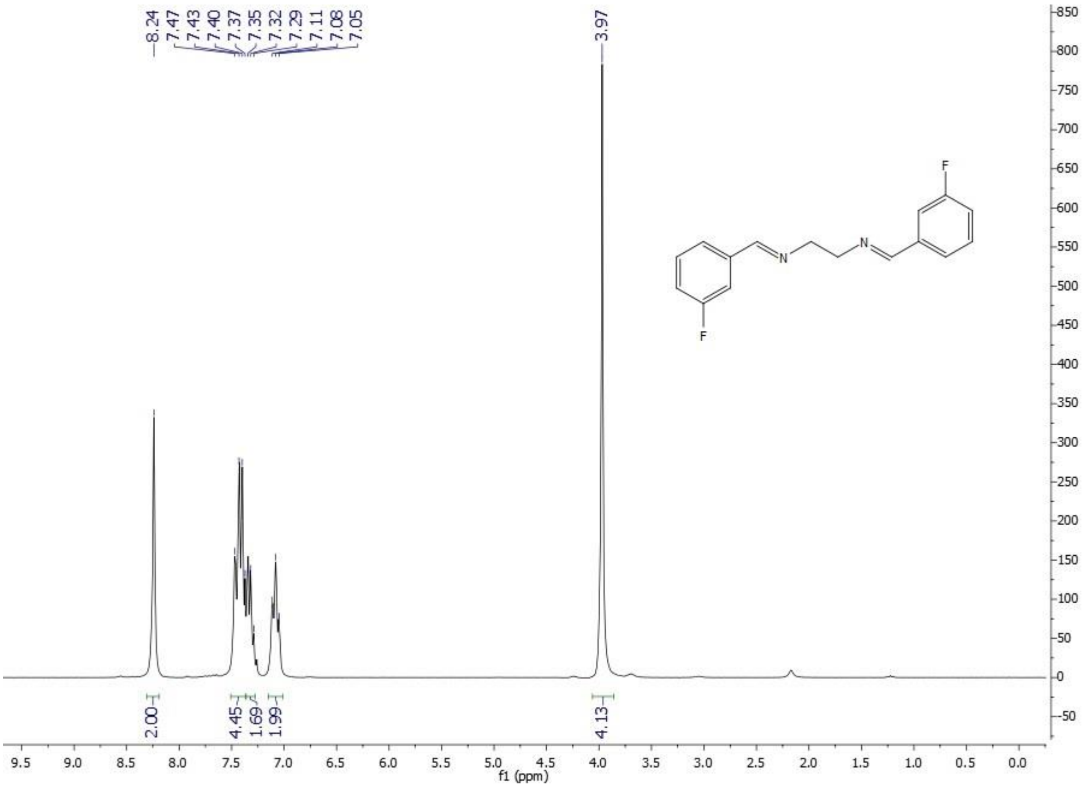

161.89
134.61
133.02
131.83
128.91
127.62
125.07
77.65
77.16
77.12
76.65
76.61
61.39
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200

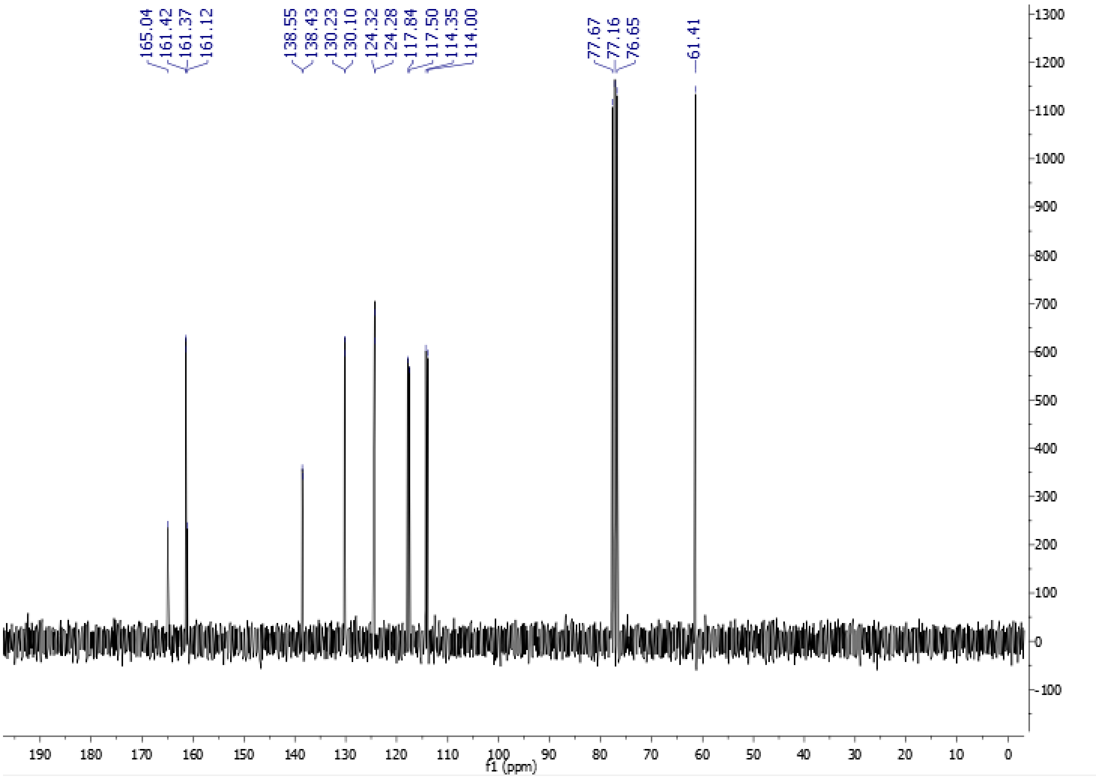
Compound **2n**


8.23
7.71
7.68
7.65
7.26
7.09
7.06
7.03
3.94
F
N
N
F
2.00
4.02
4.02
4.01
f1 (ppm)

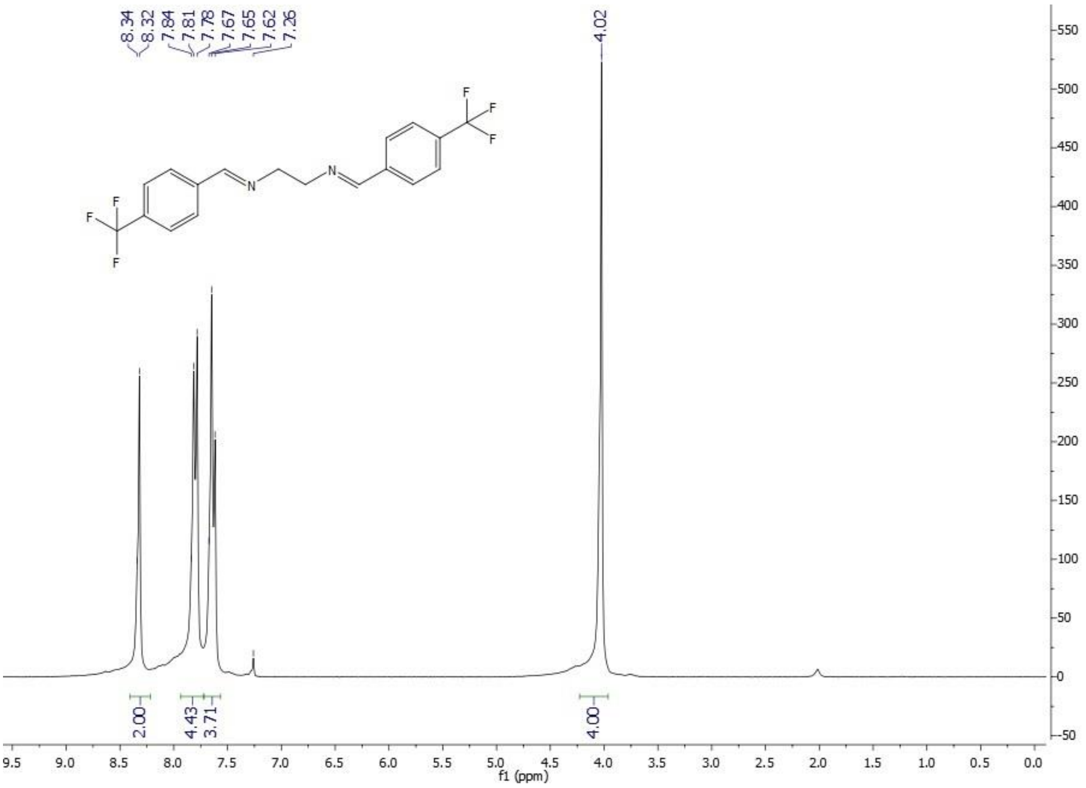

166.37
162.39
161.30
132.56
132.51
130.12
129.99
115.94
115.59
77.67
77.16
76.65
61.59
f1 (ppm)

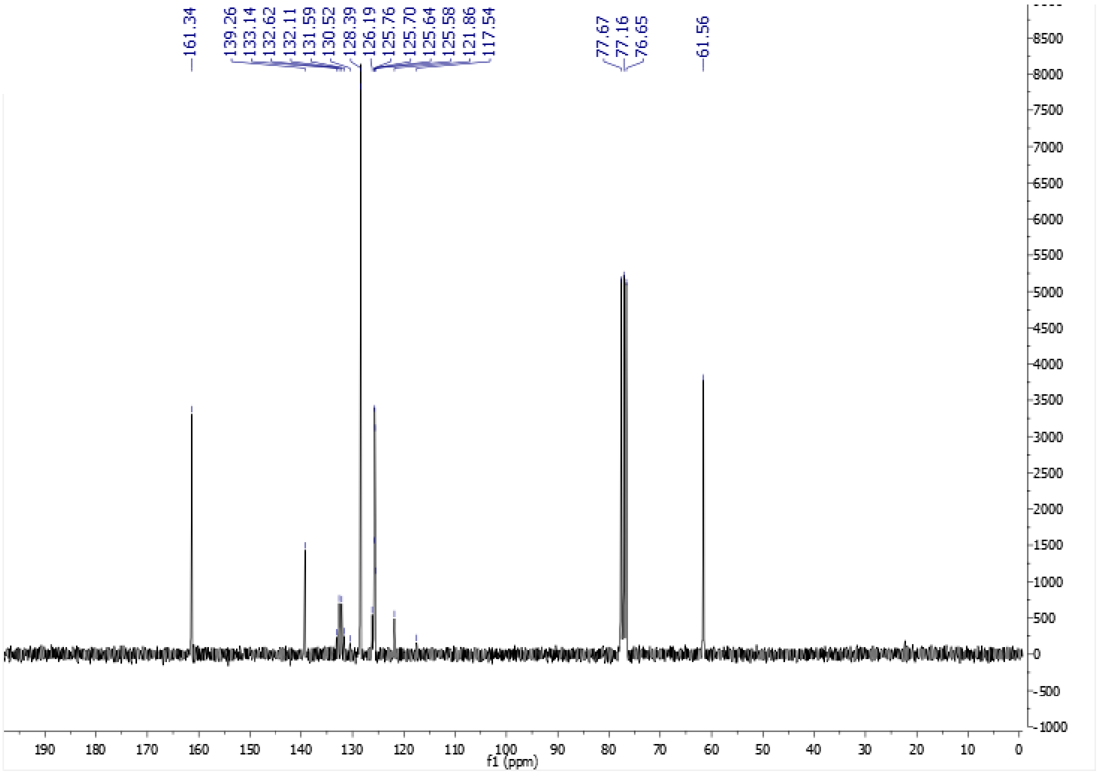
Compound **2o**


8.24
7.47
7.43
7.40
7.37
7.35
7.32
7.29
7.11
7.08
7.05
3.97
2.00
4.45
1.69
1.99
4.13
F
N
N
F
f1 (ppm)

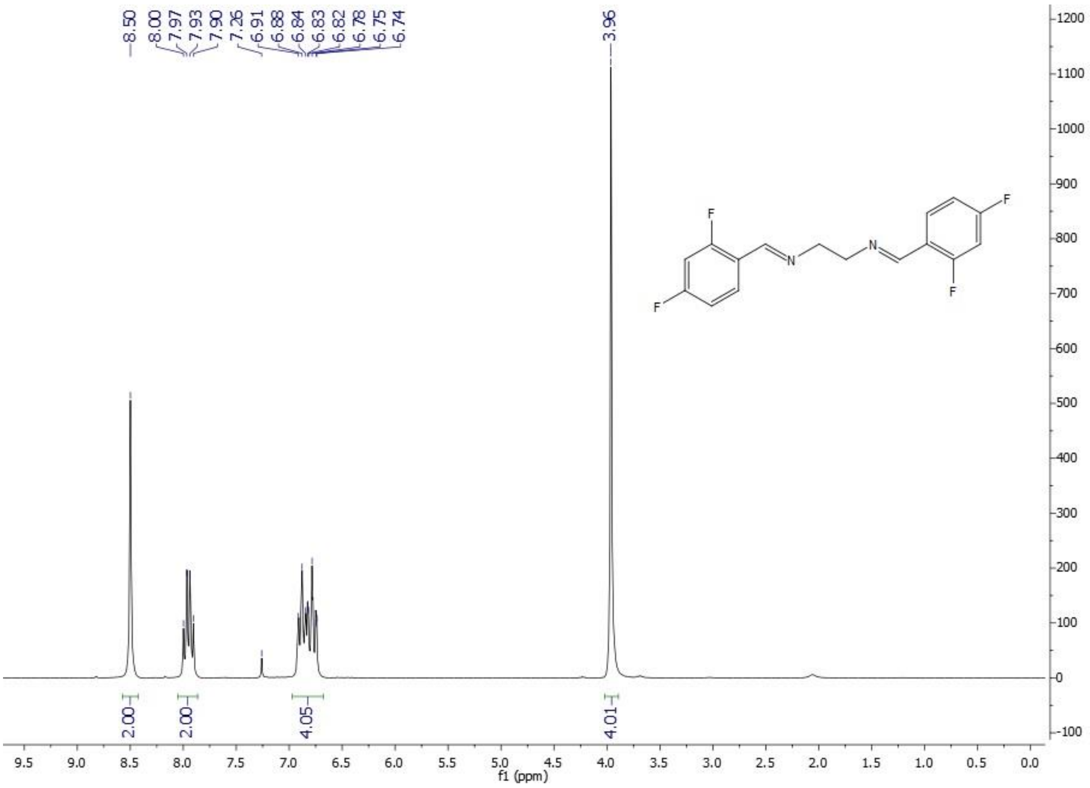

165.04
161.42
161.37
161.12
138.55
138.43
130.23
130.10
124.32
124.28
117.84
117.50
114.35
114.00
77.67
77.16
76.65
61.41
f1 (ppm)

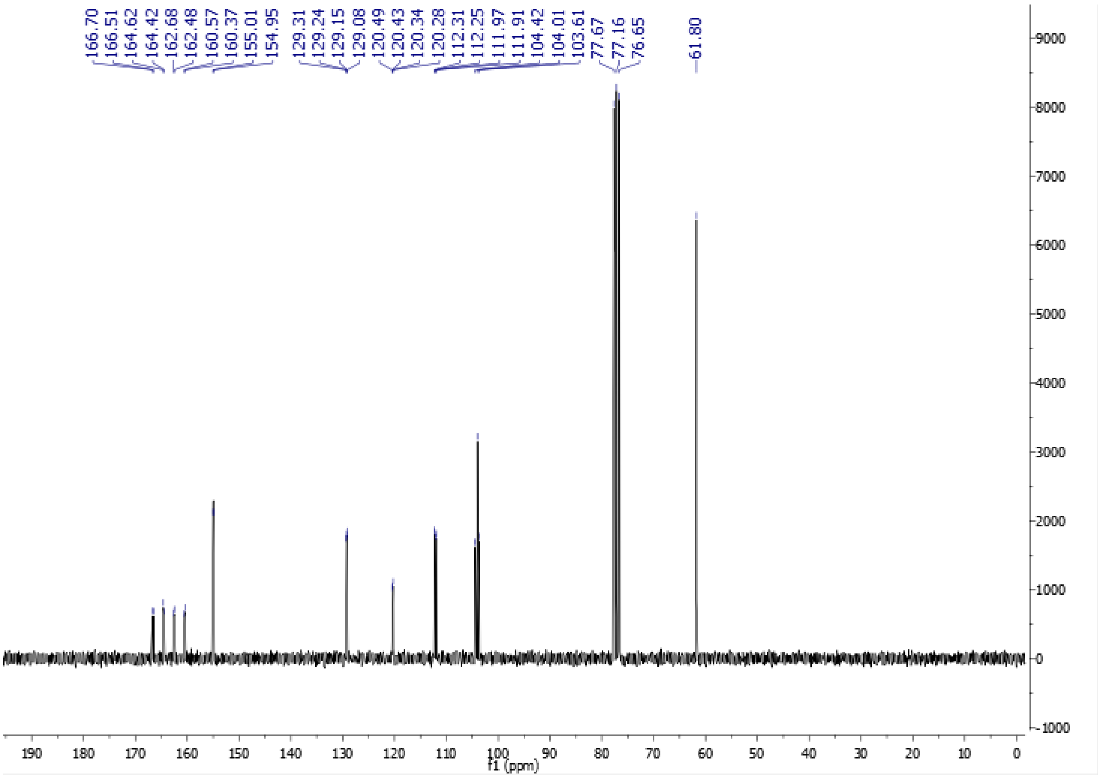
Compound **2p**


8.34
8.32
7.84
7.81
7.78
7.67
7.65
7.62
7.26
4.02
F
F
F
N
N
F
F
F
2.00
4.43
3.71
4.00
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
f1 (ppm)
550
500
450
400
350
300
250
200
150
100
50
0
-50

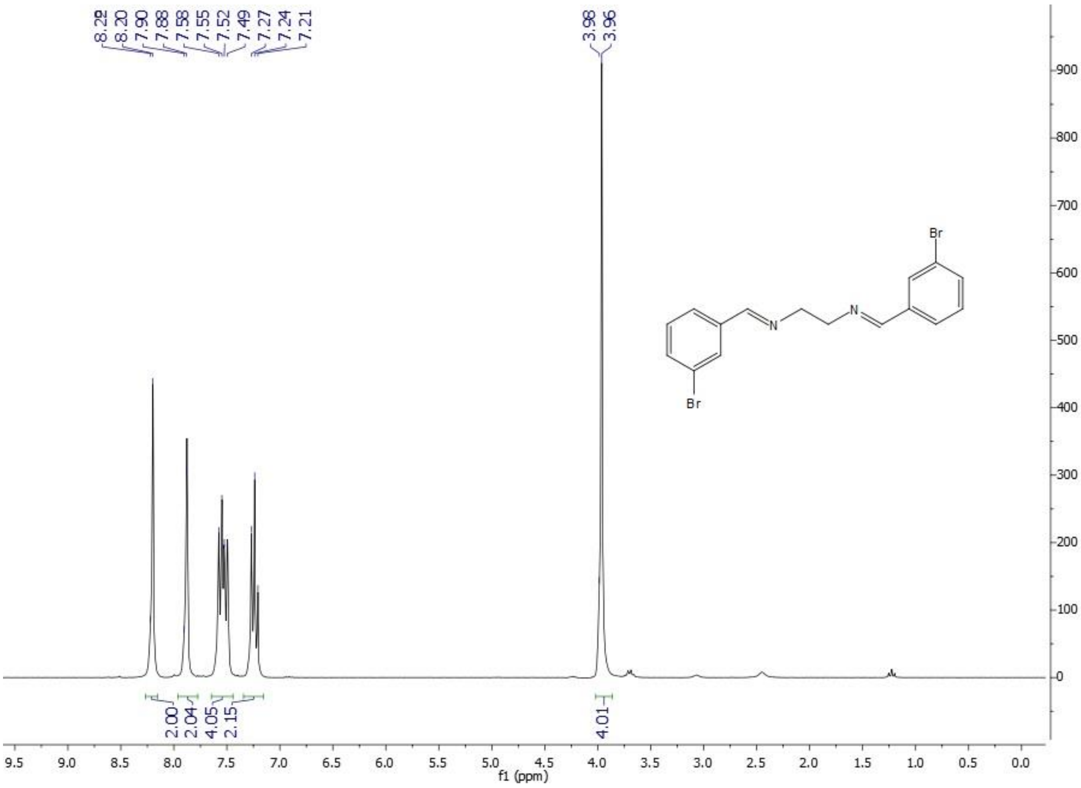

161.34
139.26
133.14
132.62
132.11
131.59
130.52
128.39
126.19
125.76
125.70
125.64
125.58
121.86
117.54
77.67
77.16
76.65
61.56
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000

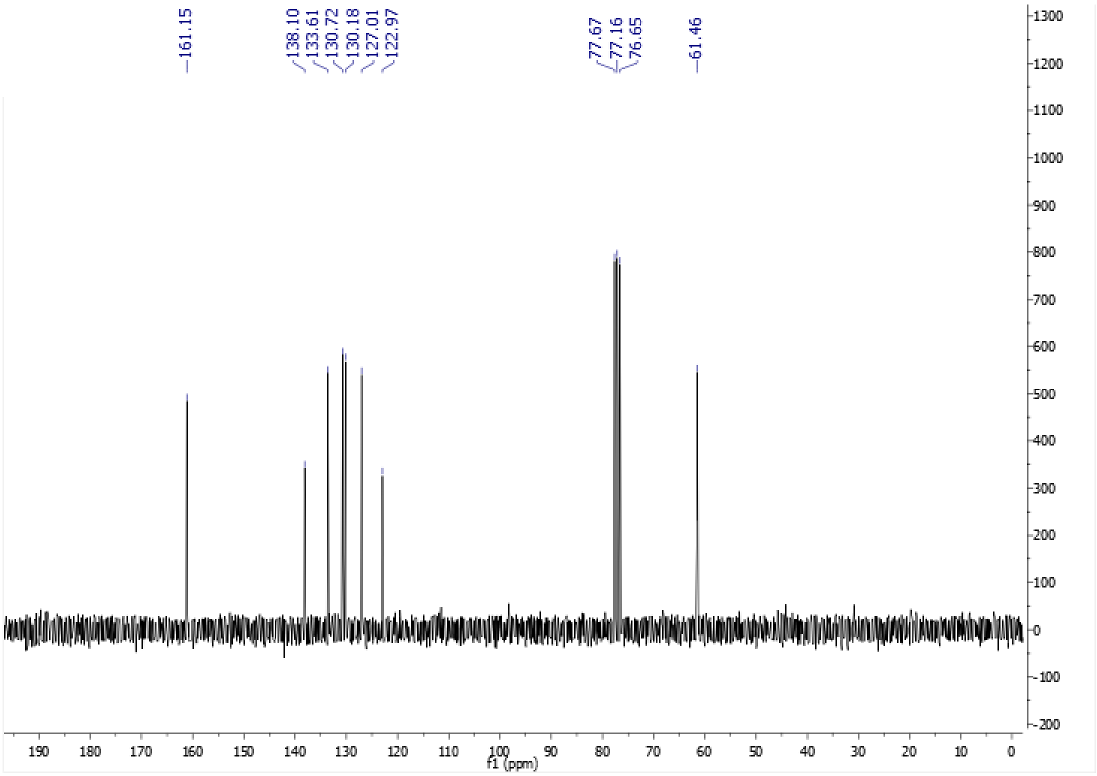
Compound **2q**


8.50
8.00
7.97
7.93
7.90
7.26
6.91
6.88
6.84
6.83
6.82
6.78
6.75
6.74
3.96
2.00
2.00
4.05
4.01
F
F
N
N
F
F
f1 (ppm)

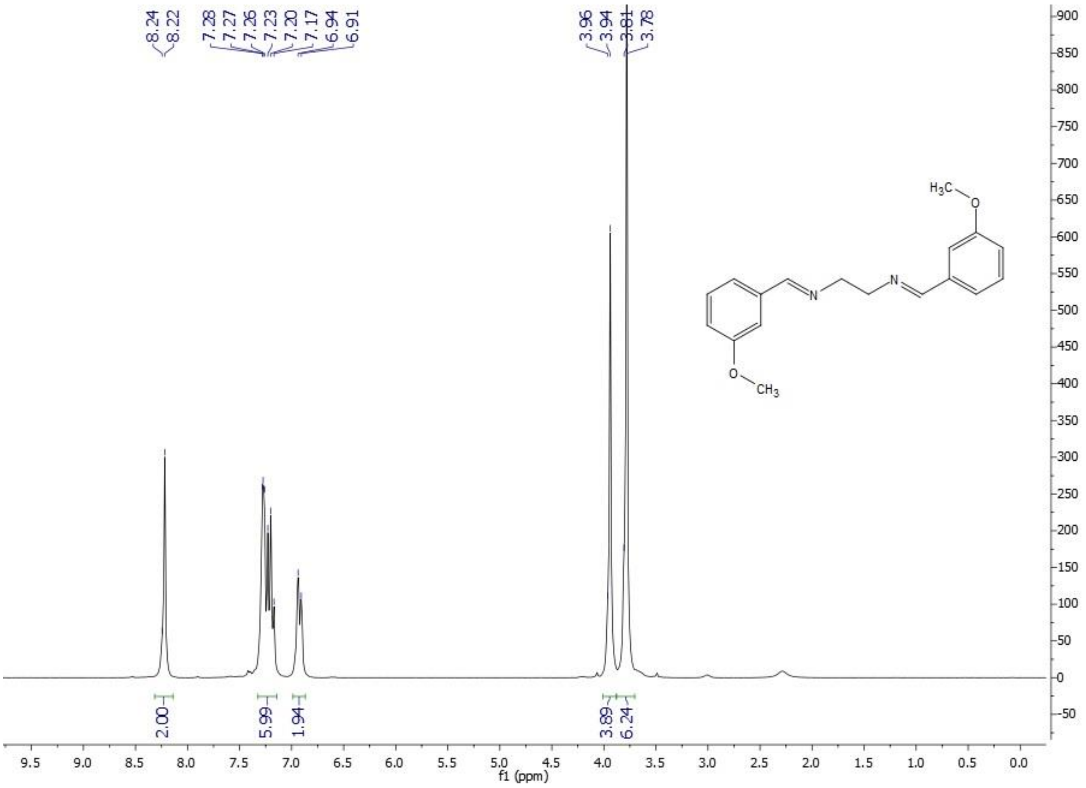

166.70
166.51
164.62
164.42
162.68
162.48
160.57
160.37
155.01
154.95
129.31
129.24
129.15
129.08
120.49
120.43
120.34
120.28
112.31
112.25
111.97
111.91
104.42
104.01
103.61
77.67
77.16
76.65
61.80
f1 (ppm)

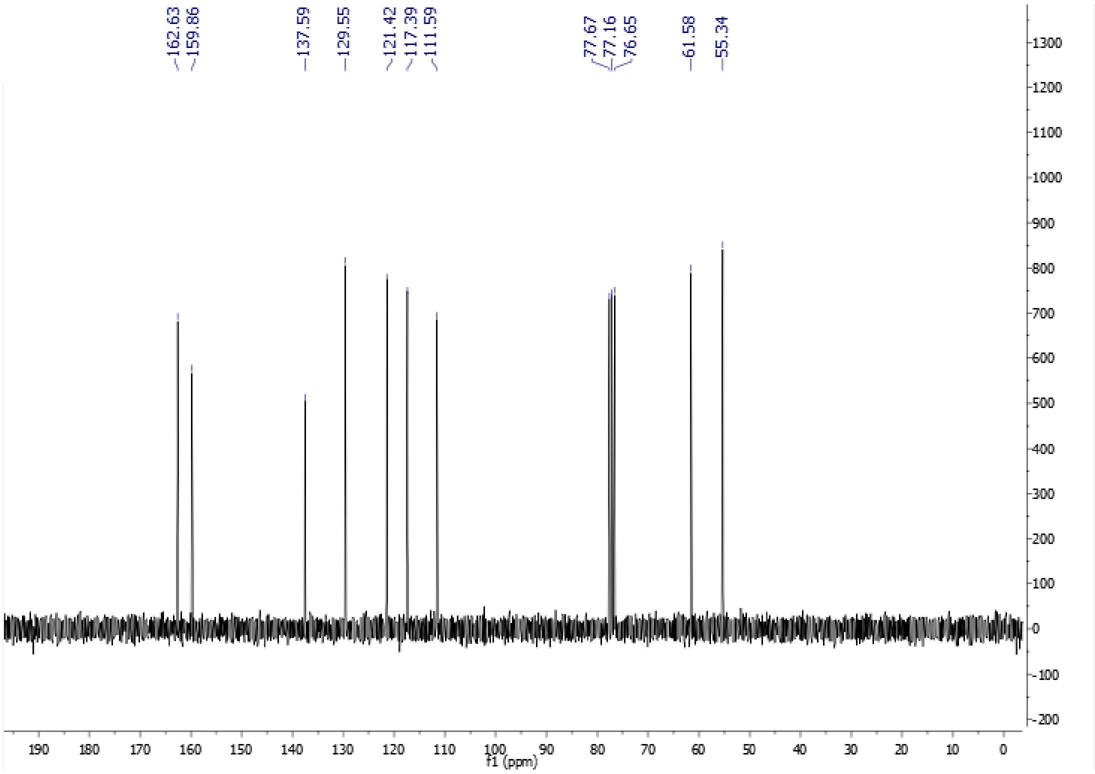
Compound **2r**


8.22
8.20
7.90
7.88
7.58
7.55
7.52
7.49
7.27
7.24
7.21
3.98
3.96
Br
N
N
Br
2.00
2.04
4.05
2.15
4.01
f1 (ppm)


161.15
138.10
133.61
130.72
130.18
127.01
122.97
77.67
77.16
76.65
61.46
f1 (ppm)

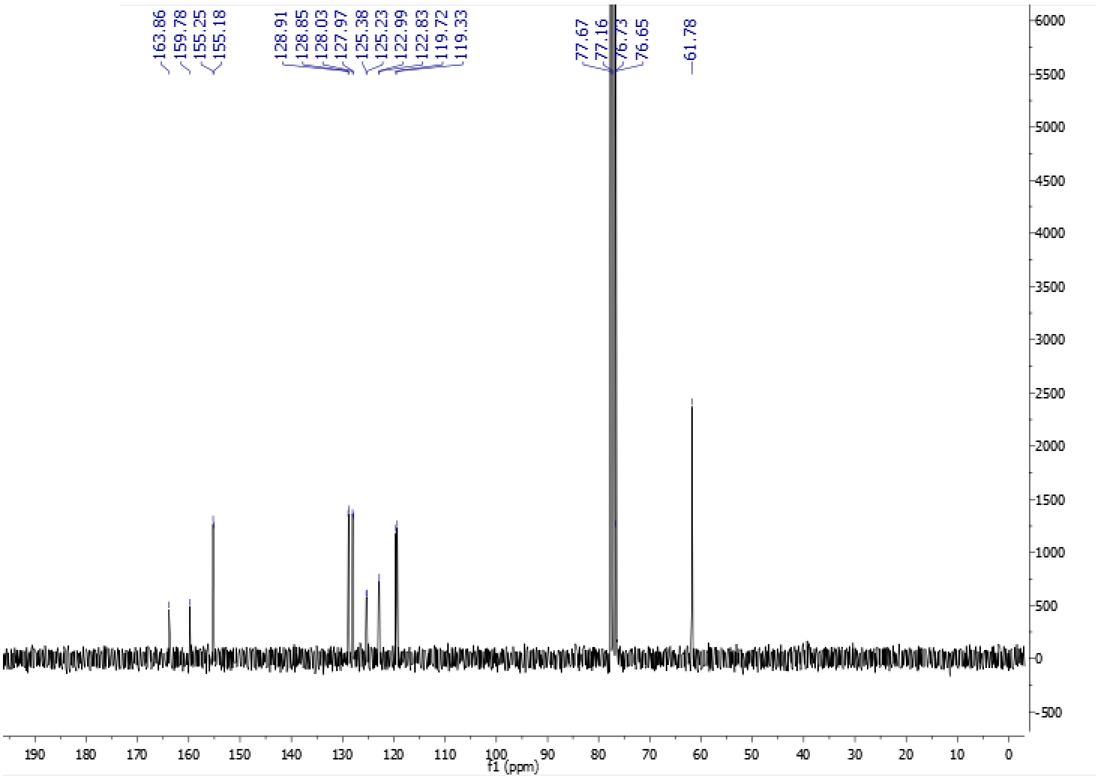
Compound **2s**


8.24
8.22
7.28
7.27
7.26
7.23
7.20
7.17
6.94
6.91
3.96
3.94
3.81
3.78
2.00
5.99
1.94
3.89
6.24
H3C
O
N
N
O
CH3
f1 (ppm)


162.63
159.86
137.59
129.55
121.42
117.39
111.59
77.67
77.16
76.65
61.58
55.34
f1 (ppm)

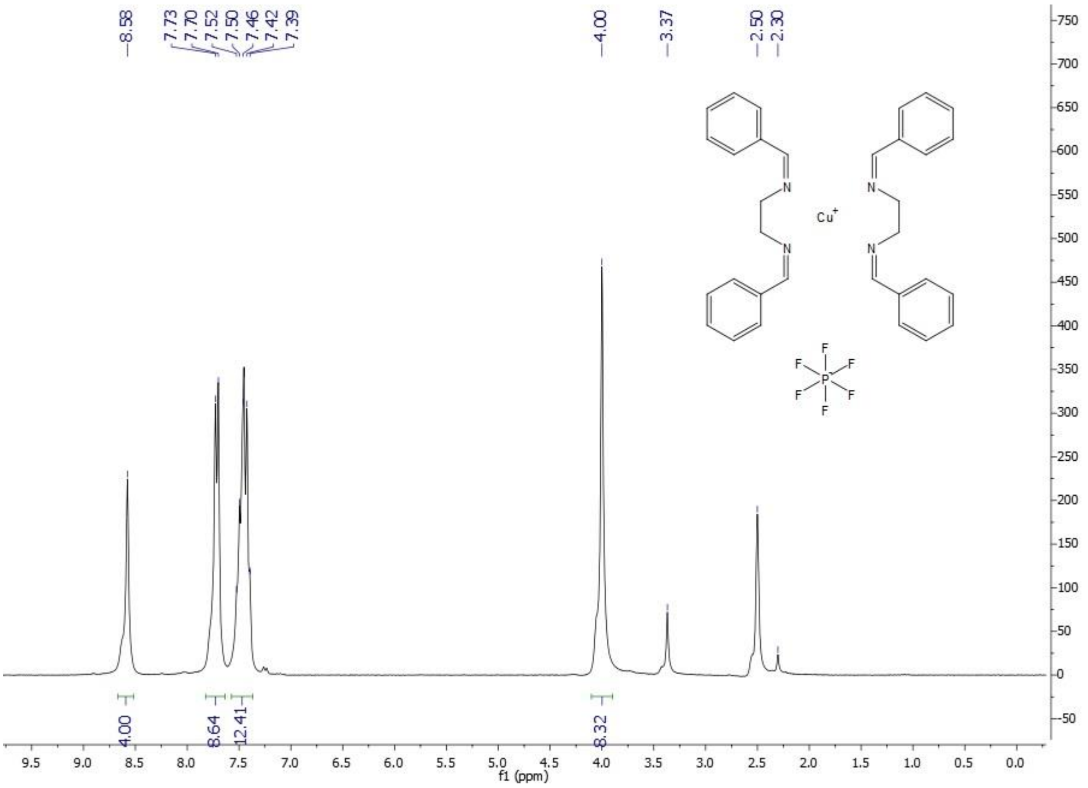
Compound **2t**

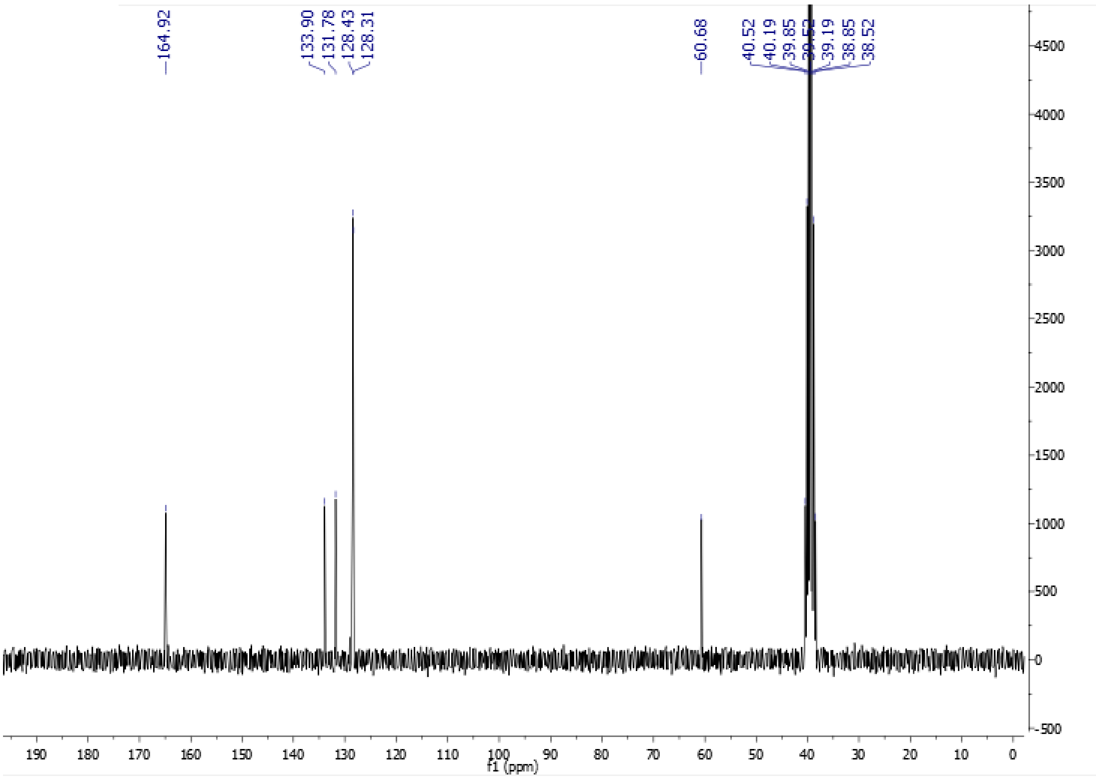
8.50
7.85
7.82
7.78
7.31
7.27
7.26
7.23
3.97
1.79
2.00
2.01
4.63
4.01
F
Br
N
N
Br
F
f1 (ppm)



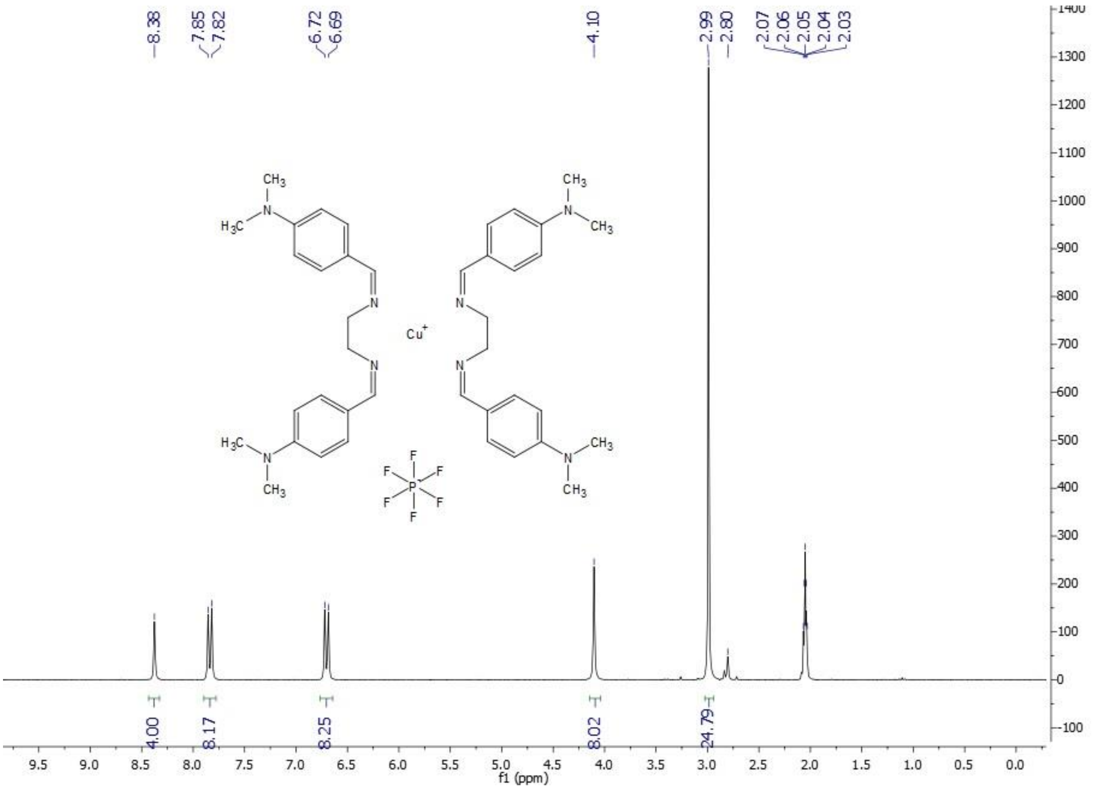
163.86
159.78
155.25
155.18
128.91
128.85
128.03
127.97
125.38
125.23
122.99
122.83
119.72
119.33
77.67
77.16
76.73
76.65
61.78
f1 (ppm)

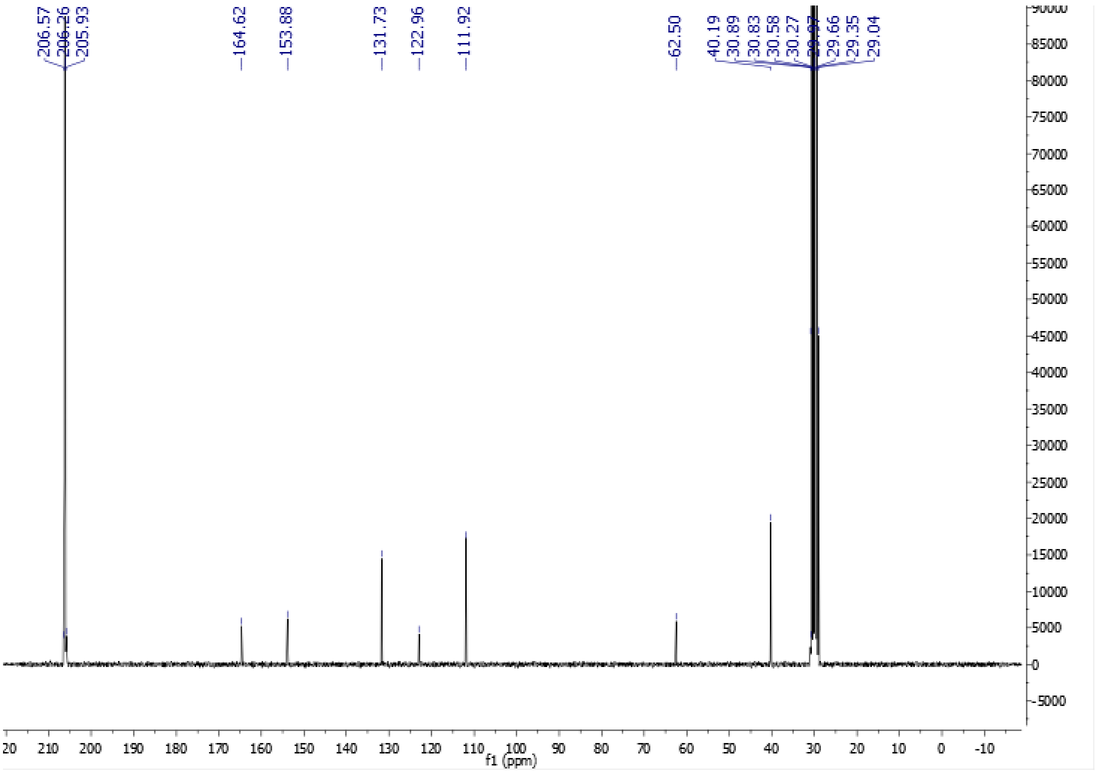
Compound **6a**


8.58
7.73
7.70
7.52
7.50
7.46
7.42
7.39
4.00
3.37
2.50
2.30
4.00
8.64
12.41
8.32
f1 (ppm)
Cu+
N
F
P

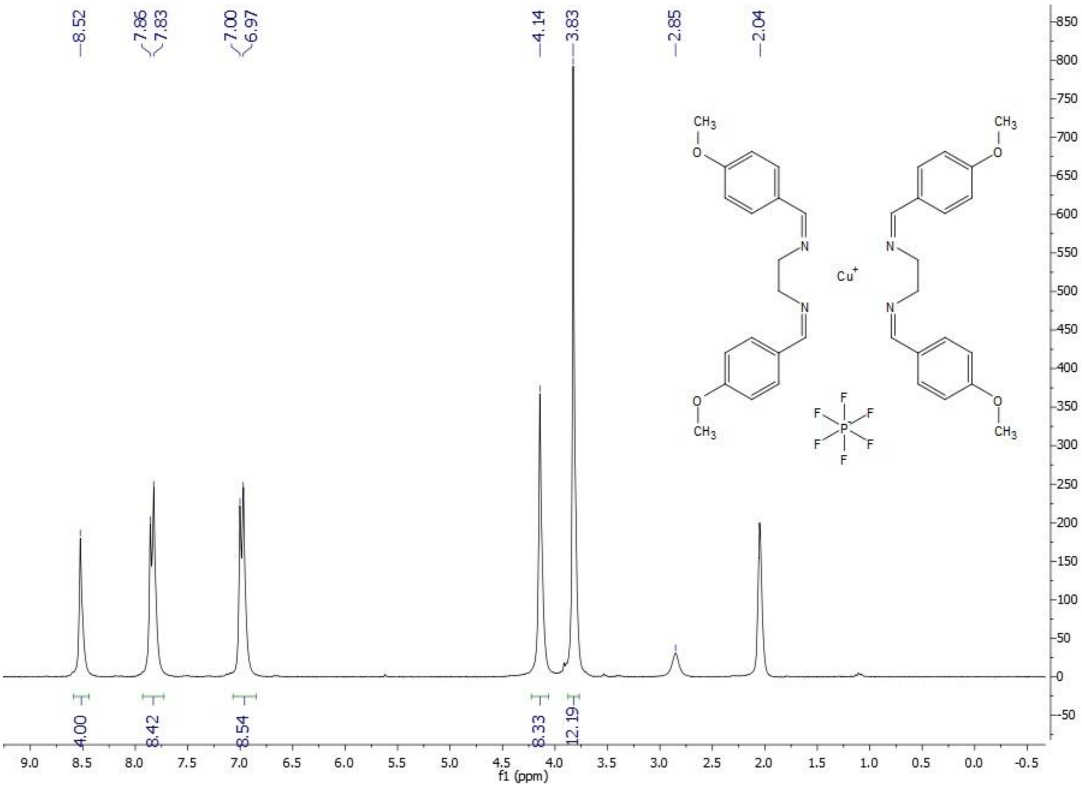

164.92
133.90
131.78
128.43
128.31
60.68
40.52
40.19
39.85
39.52
39.19
38.85
38.52
f1 (ppm)

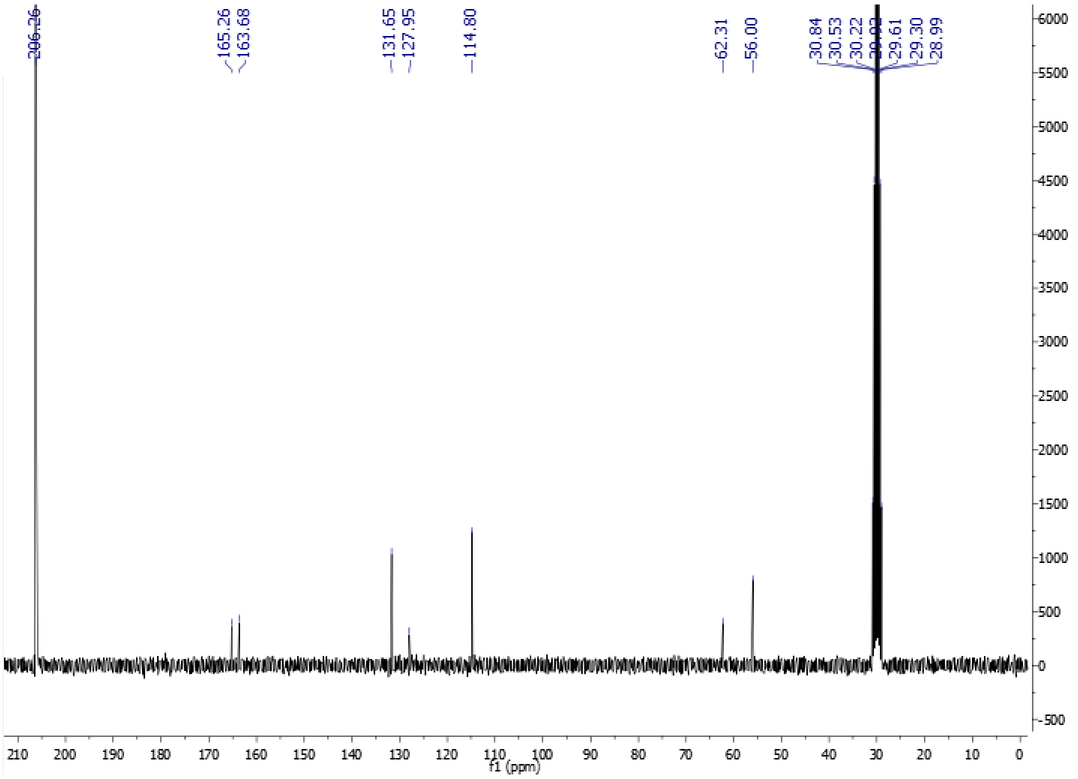
Compound **6b**


8.38
7.85
7.82
6.72
6.69
4.10
2.99
2.80
2.07
2.06
2.05
2.04
2.03
CH3
H3C
N
Cu+
F
P
4.00
8.17
8.25
8.02
24.79
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
f1 (ppm)
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

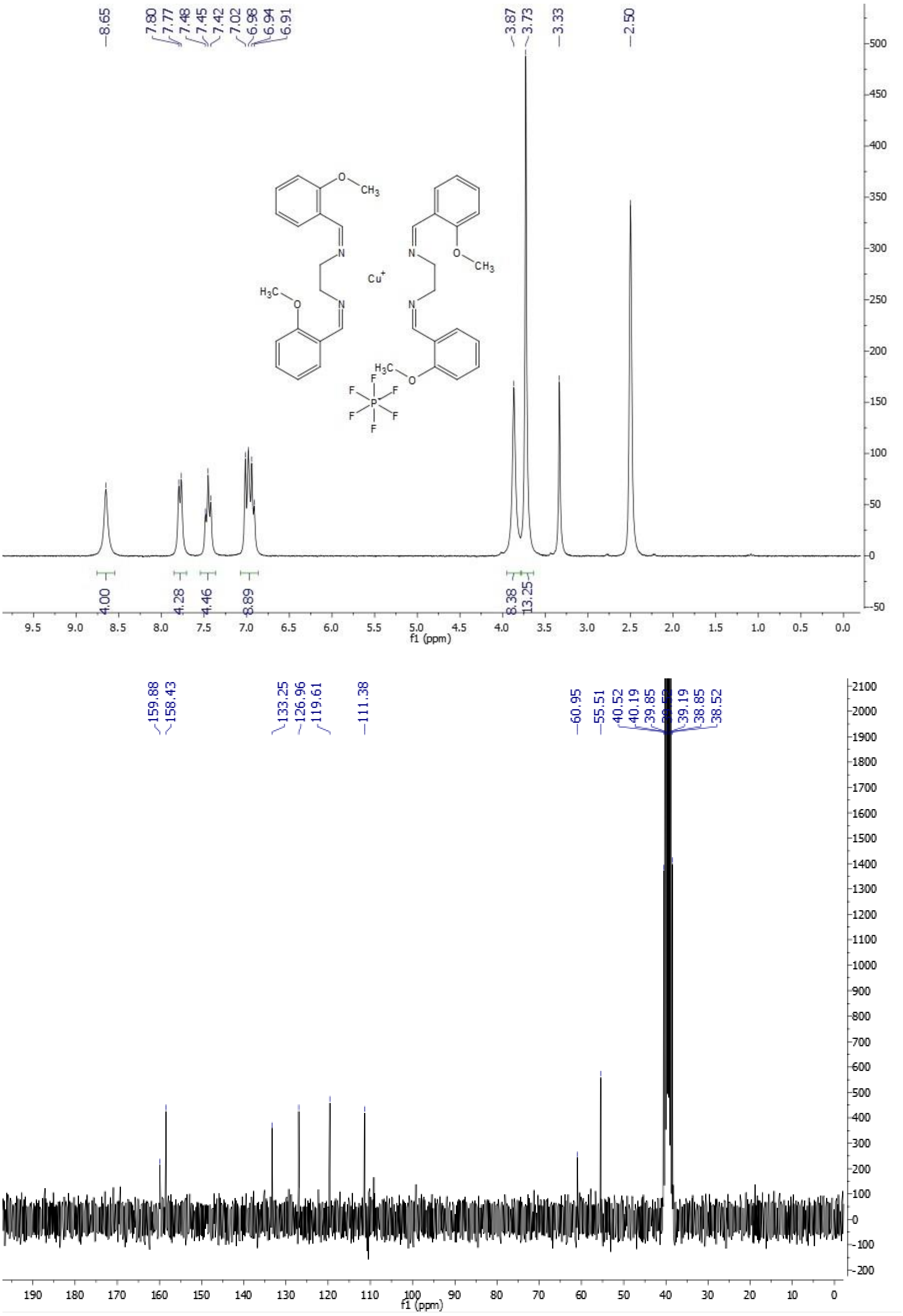

206.57
206.26
205.93
164.62
153.88
131.73
122.96
111.92
62.50
40.19
30.89
30.83
30.58
30.27
29.97
29.66
29.35
29.04
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
90000
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

Compound **6c**

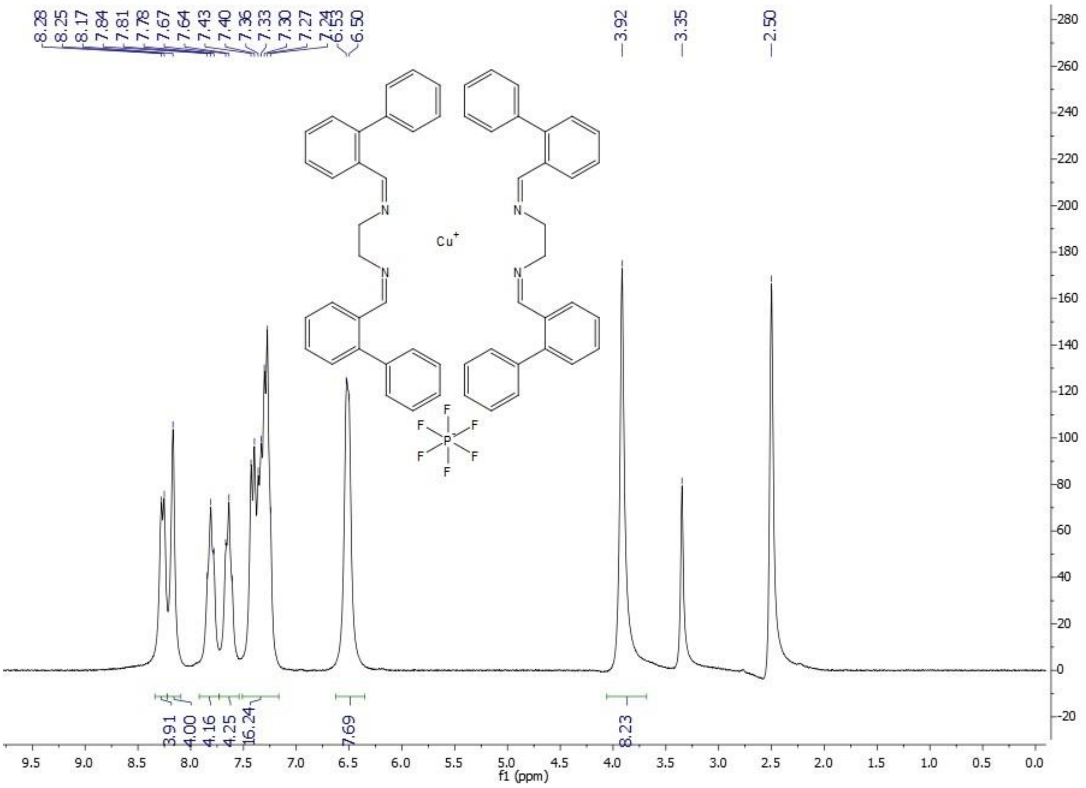

8.52
7.86
7.83
7.00
6.97
4.14
3.83
2.85
2.04
CH3
O
N
Cu+
F
P
4.00
8.42
8.54
8.33
12.19
f1 (ppm)

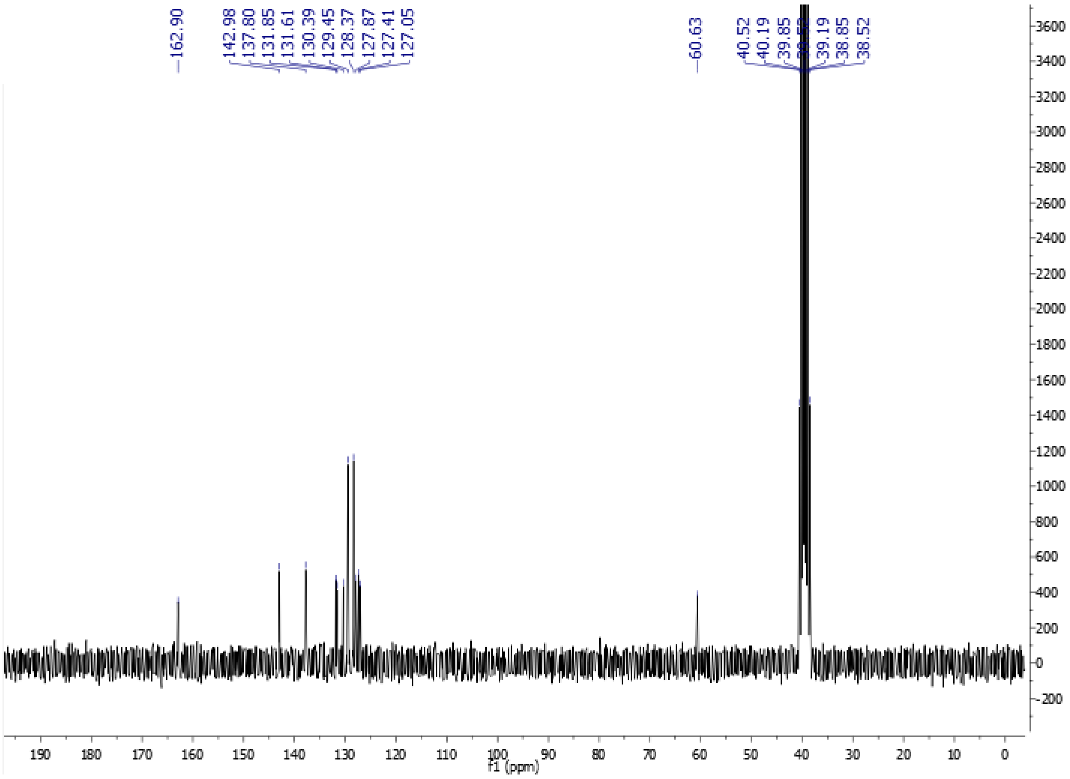

206.26
165.26
163.68
131.65
127.95
114.80
62.31
56.00
30.84
30.53
30.22
29.61
29.30
28.99
f1 (ppm)

Compound **6d**

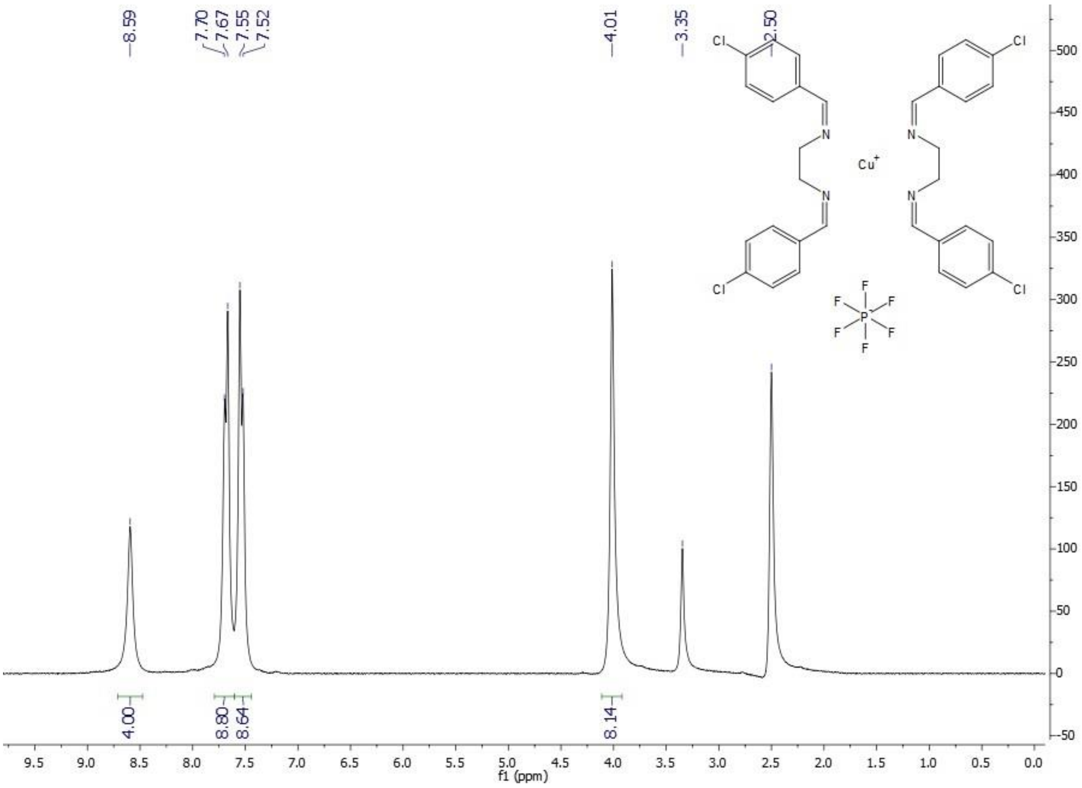

8.65
7.80
7.77
7.48
7.45
7.42
7.02
6.98
6.94
6.91
3.87
3.73
3.33
2.50
O
CH_3
N
N
Cu^+
H_3C
O
N
O
CH_3
N
H_3C
O
F
F
F
P
F
F
F
4.00
4.28
4.46
8.89
8.38
13.25
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
500
450
400
350
300
250
200
150
100
50
0
-50
159.88
158.43
133.25
126.96
119.61
111.38
60.95
55.51
40.52
40.19
39.85
39.19
38.85
38.52
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

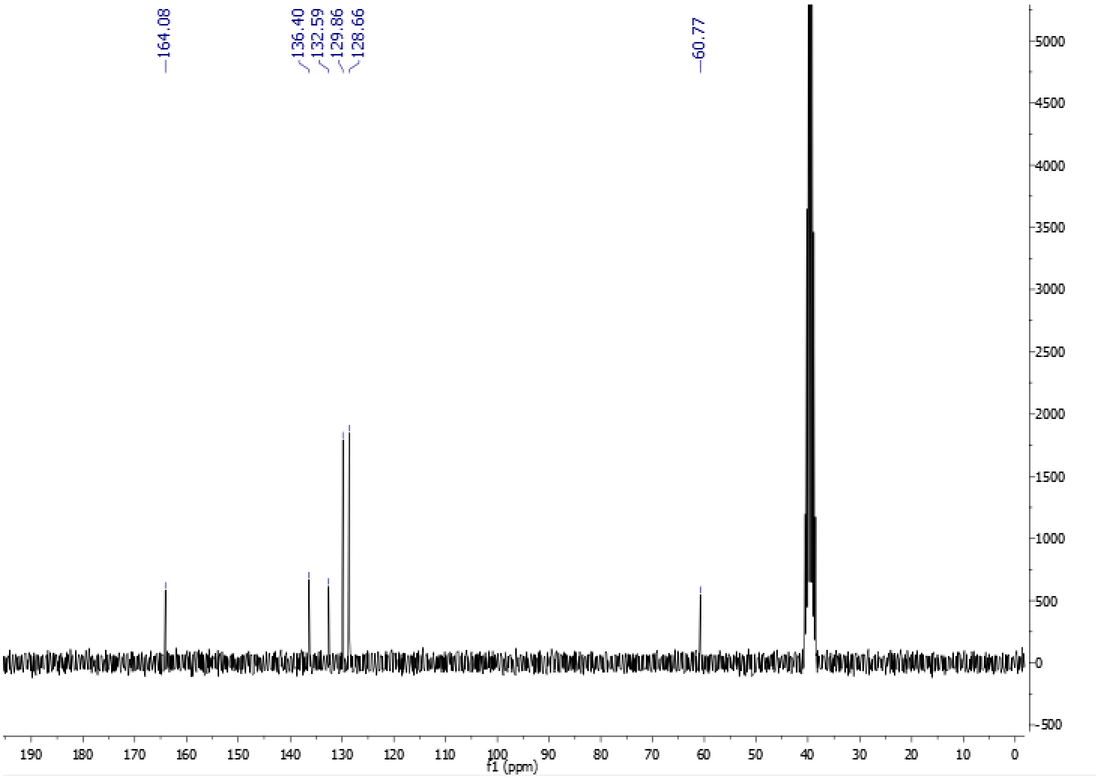
Compound **6e**


8.28
8.25
8.17
7.84
7.81
7.78
7.67
7.64
7.43
7.40
7.36
7.33
7.30
7.27
7.24
6.53
6.50
3.92
3.35
2.50
Cu+
N
N
N
N
F
F
F
P
F
F
F
3.91
4.00
4.16
4.25
16.24
7.69
8.23
f1 (ppm)
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
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

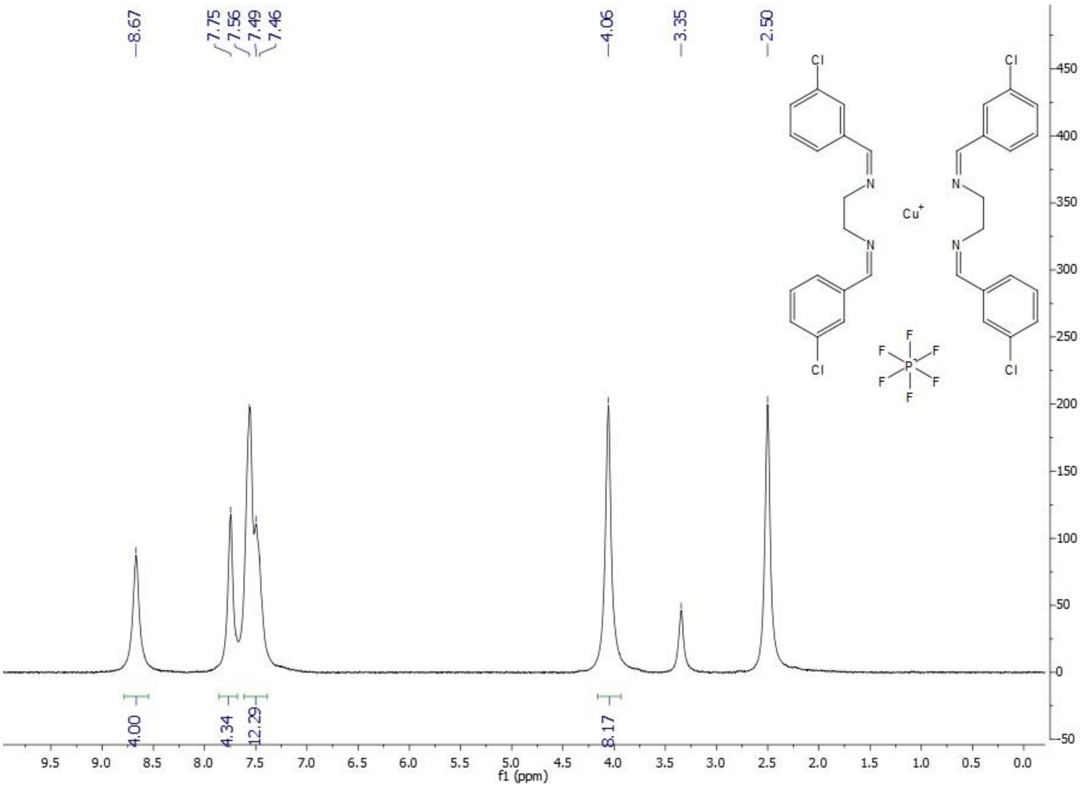

162.90
142.98
137.80
131.85
131.61
130.39
129.45
128.37
127.87
127.41
127.05
60.63
40.52
40.19
39.85
39.19
38.85
38.52
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

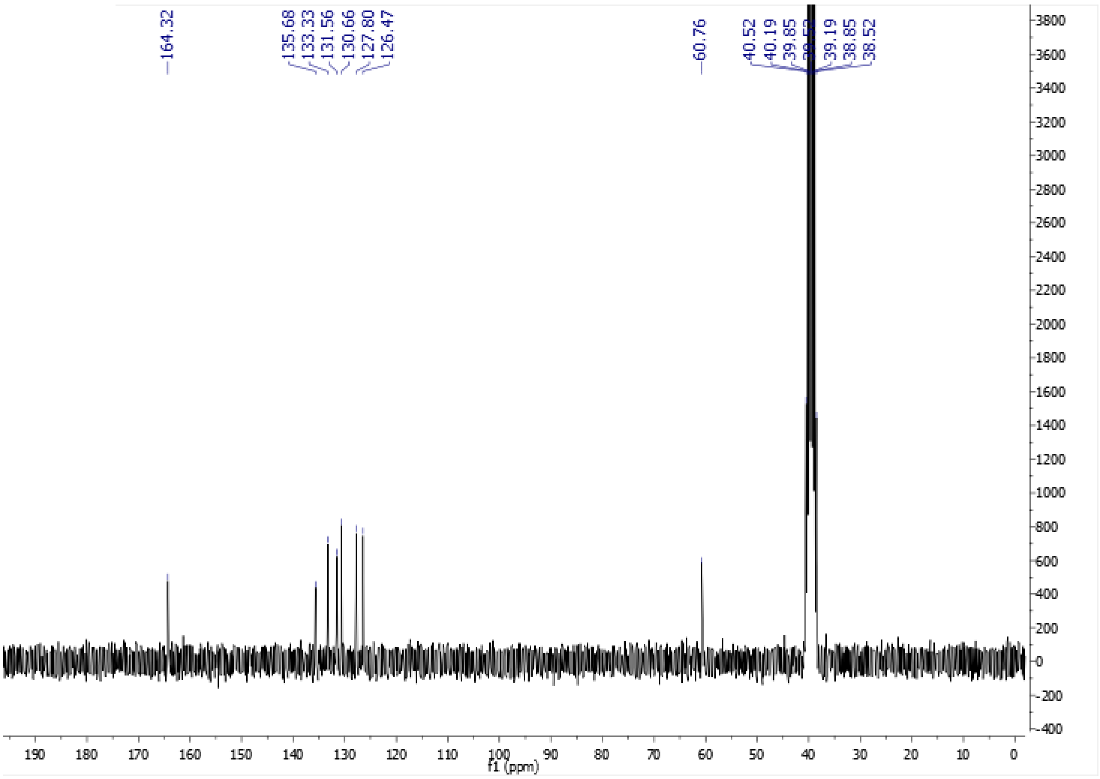
Compound **6f**


8.59
7.70
7.67
7.55
7.52
4.01
3.35
2.50
Cl
N
Cu+
F
P
4.00
8.80
8.64
8.14
500
450
400
350
300
250
200
150
100
50
0
-50
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
f1 (ppm)

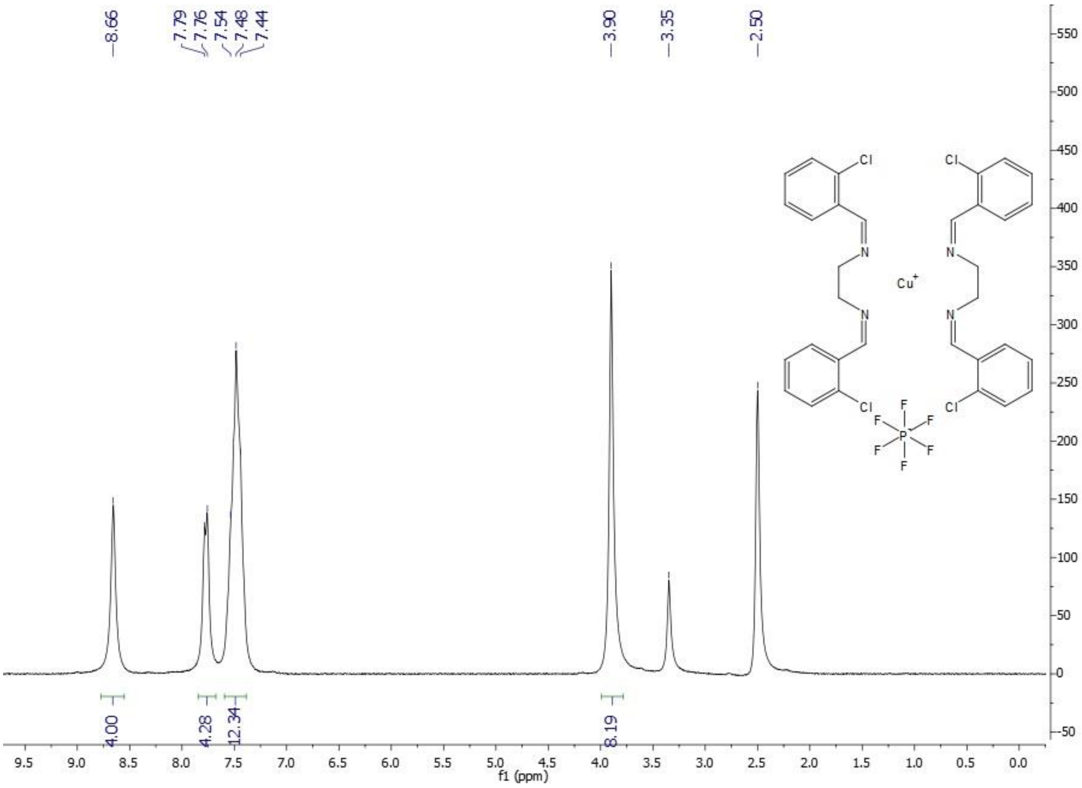

164.08
136.40
132.59
129.86
128.66
60.77
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Compound **6g**

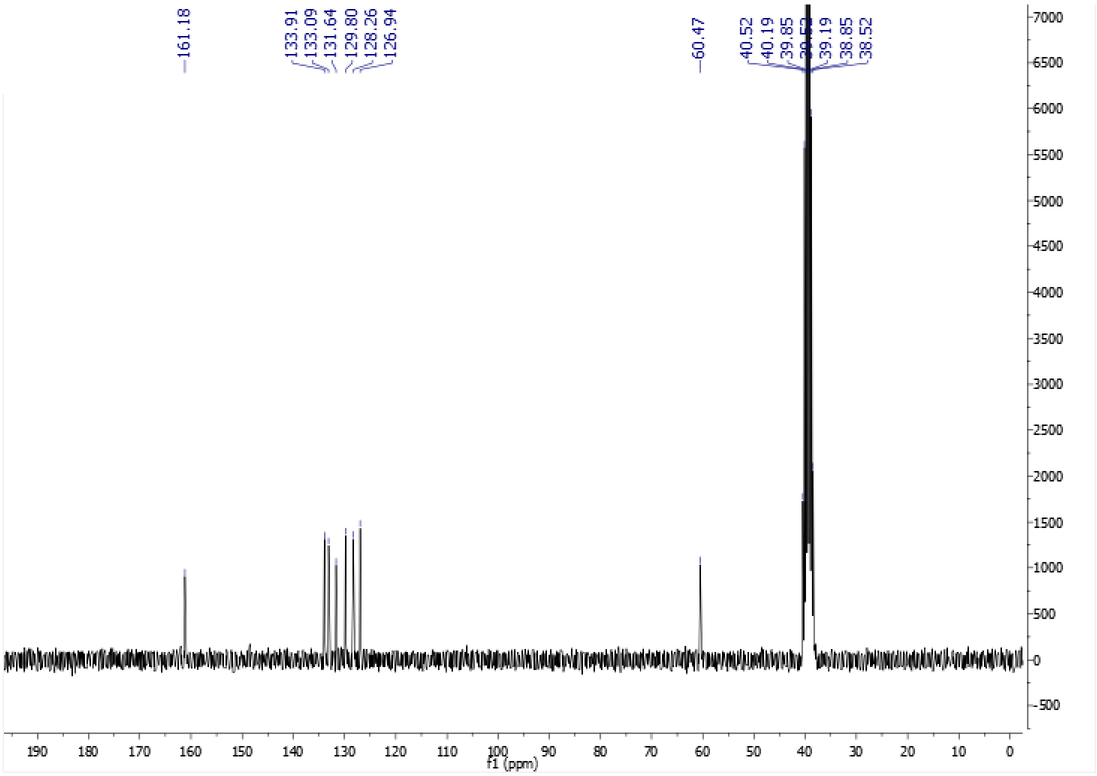

8.67
7.75
7.56
7.49
7.46
4.06
3.35
2.50
4.00
4.34
12.29
8.17
Cl
N
Cu+
F
P
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
450 400 350 300 250 200 150 100 50 0 -50


164.32
135.68
133.33
131.56
130.66
127.80
126.47
60.76
40.52
40.19
39.85
39.52
39.19
38.85
38.52
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200 -400

Compound **6h**

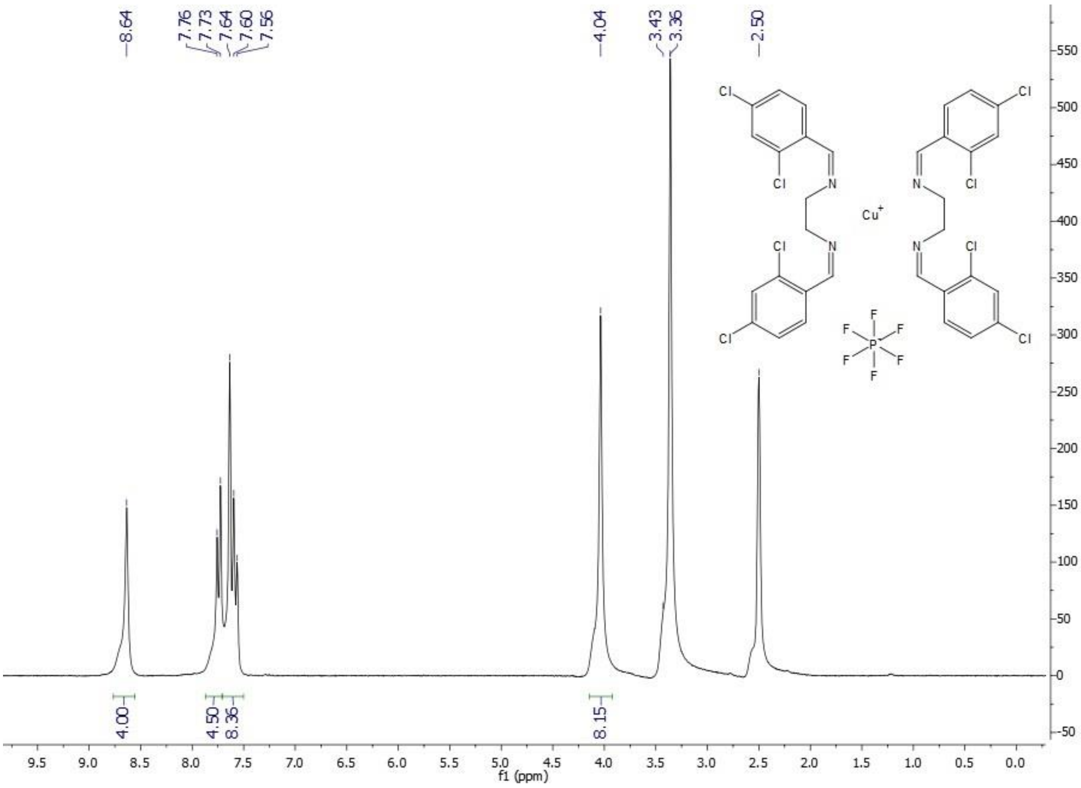


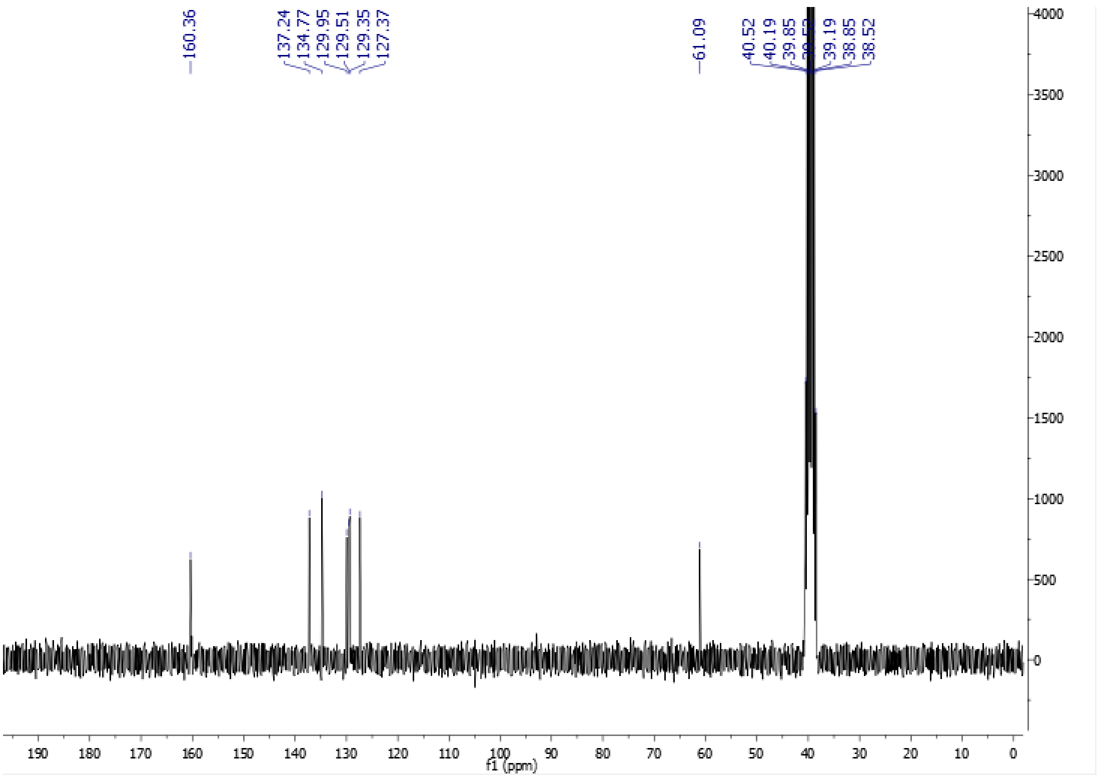
8.66
7.79
7.76
7.54
7.48
7.44
3.90
3.35
2.50
Cl
Cl
N
N
Cu+
N
N
Cl
Cl
F
F
F
P
F
F
F
4.00
4.28
12.34
8.19
f1 (ppm)



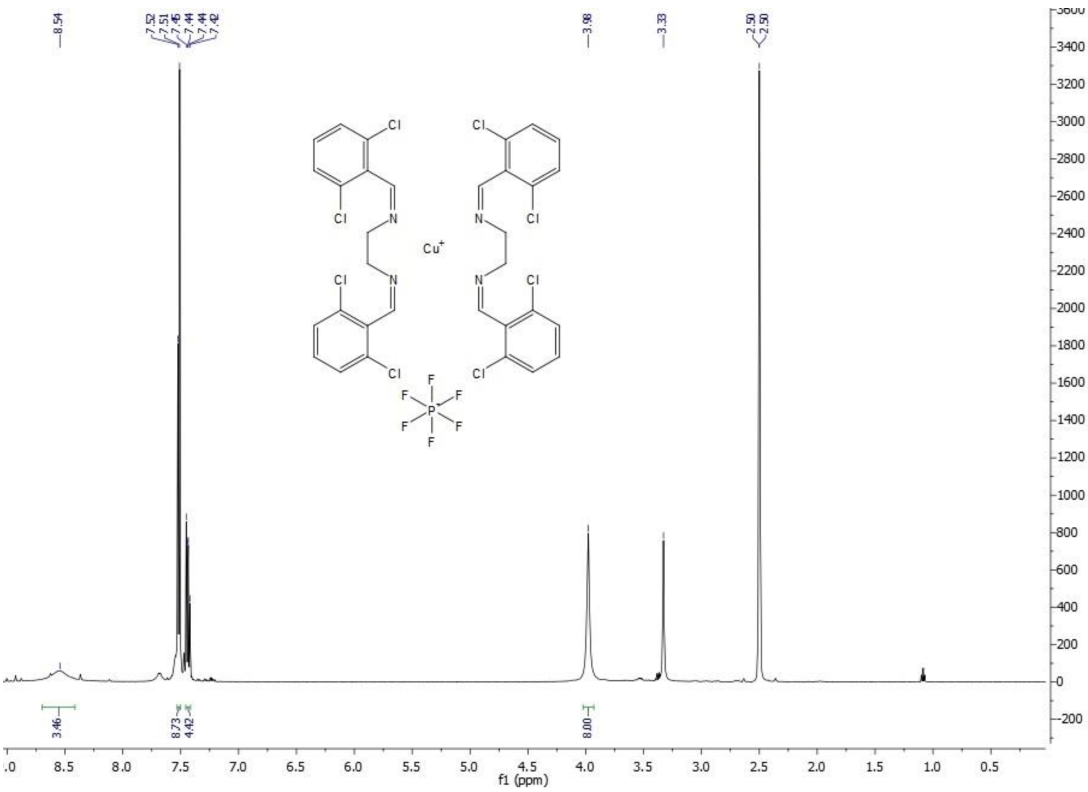
161.18
133.91
133.09
131.64
129.80
128.26
126.94
60.47
40.52
40.19
39.85
39.52
39.19
38.85
38.52
f1 (ppm)

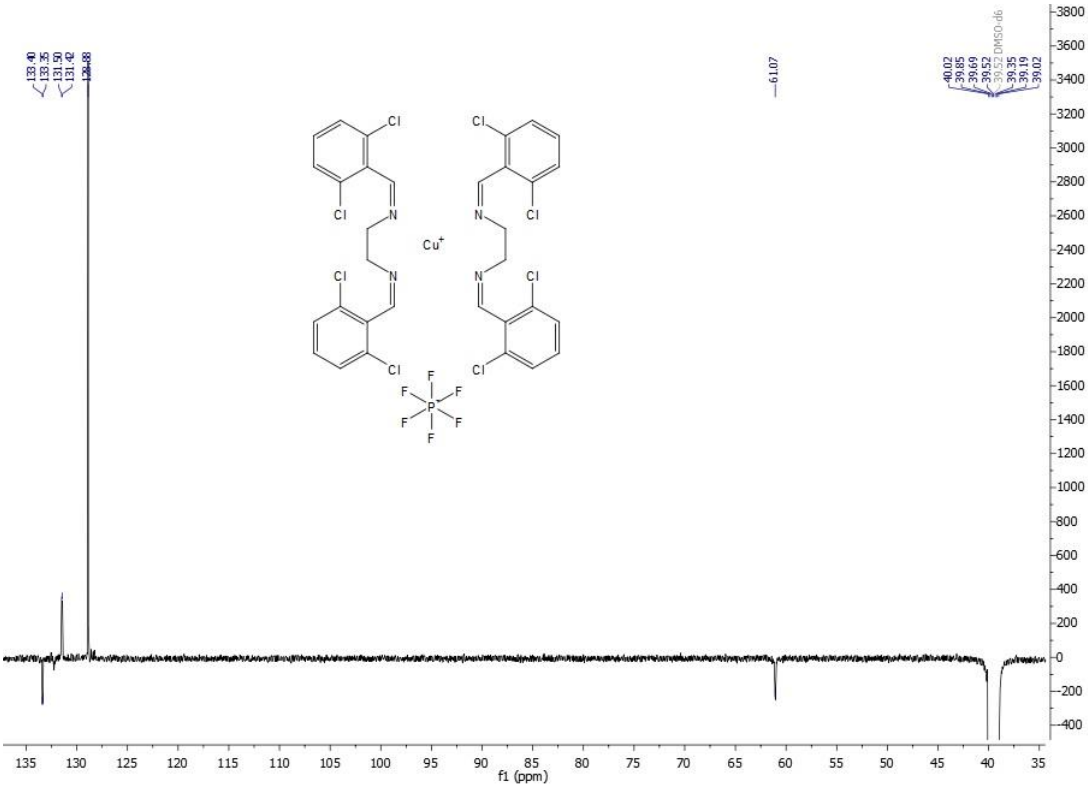
Compound **6i**

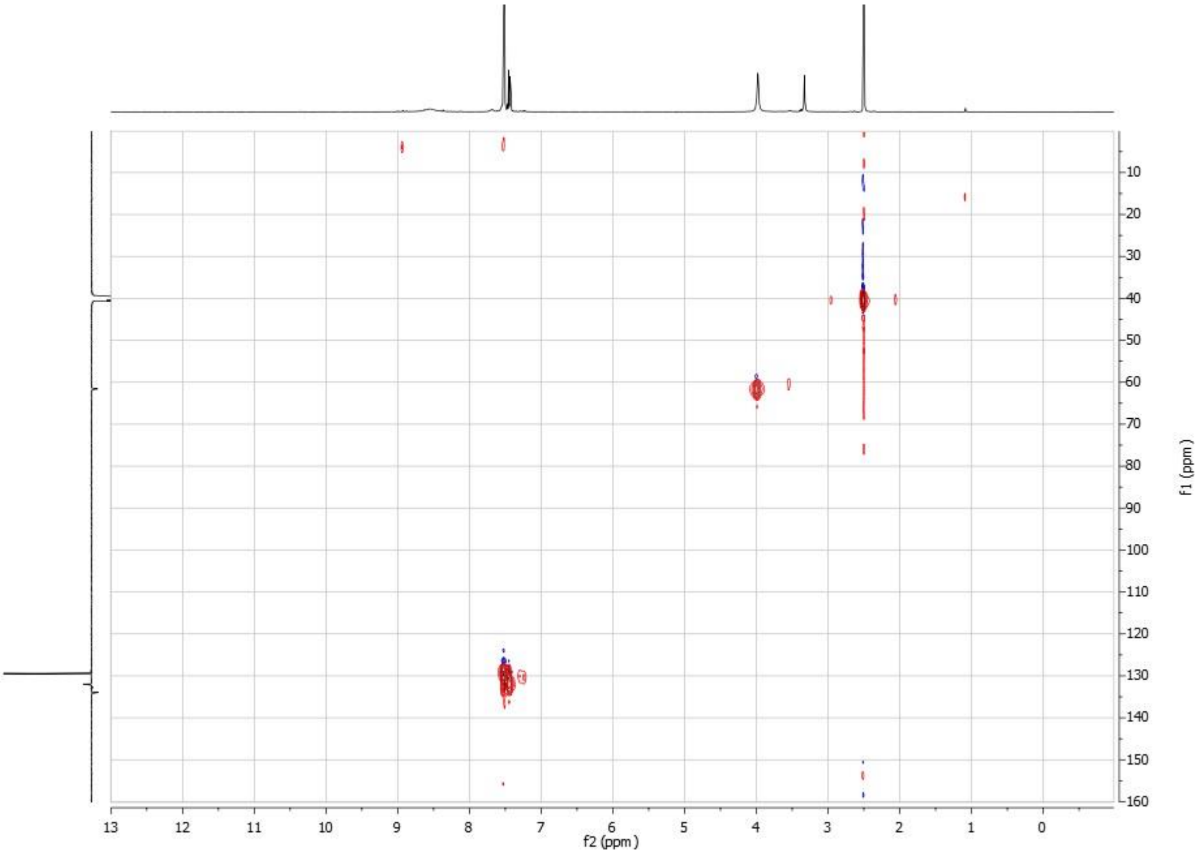

8.64
7.76
7.73
7.64
7.60
7.56
4.04
3.43
3.36
2.50
4.00
4.50
8.36
8.15
Cl
N
Cu$^+$
F
P
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
550
500
450
400
350
300
250
200
150
100
50
0
-50


160.36
137.24
134.77
129.95
129.51
129.35
127.37
61.09
40.52
40.19
39.85
39.19
38.85
38.52
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
4000
3500
3000
2500
2000
1500
1000
500
0

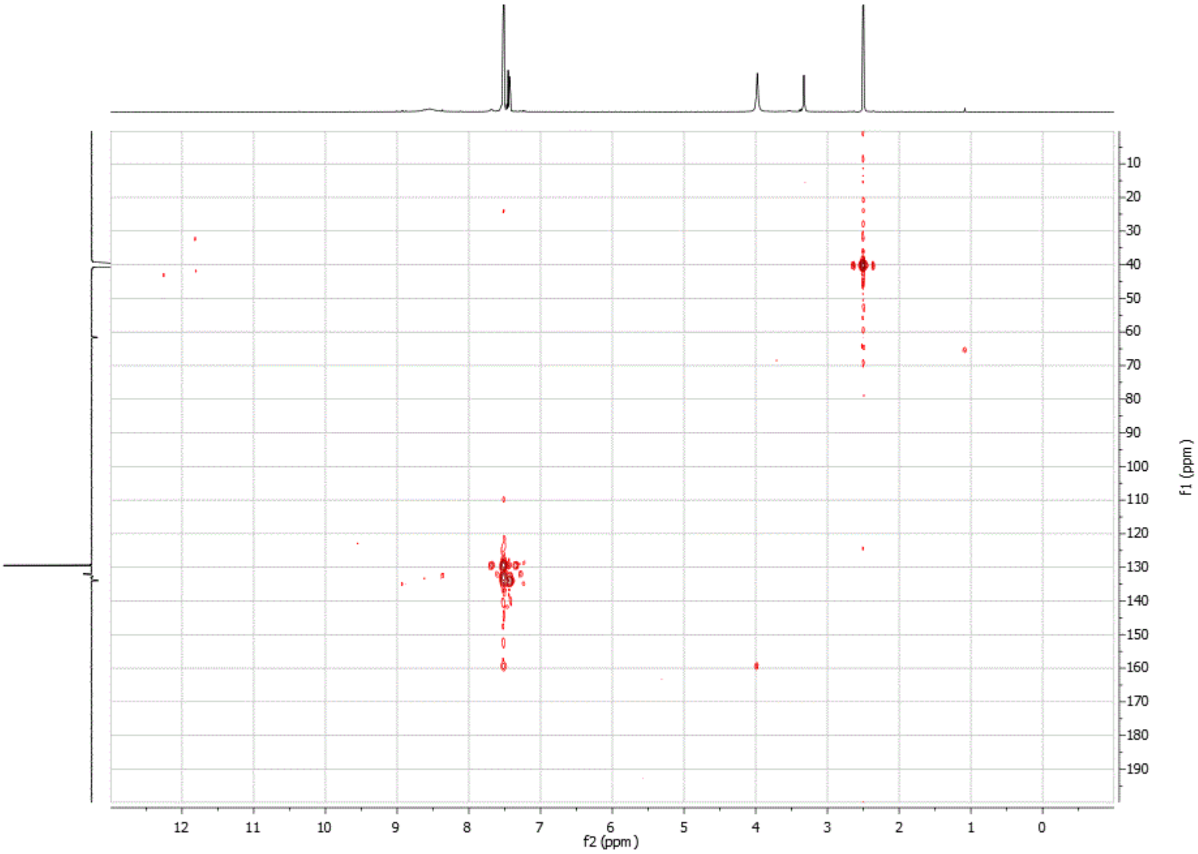
Compound **6j**


8.54
7.52
7.51
7.45
7.44
7.44
7.42
3.98
3.33
2.50
2.50
Cl
N
Cu+
F
P
3.46
8.73
4.42
8.00
f1 (ppm)
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
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200


133.40
133.35
131.50
131.42
128.88
61.07
40.02
39.85
39.69
39.52
39.52 DMSO-d6
39.35
39.19
39.02
Cl
N
Cu+
F
P
f1 (ppm)
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400

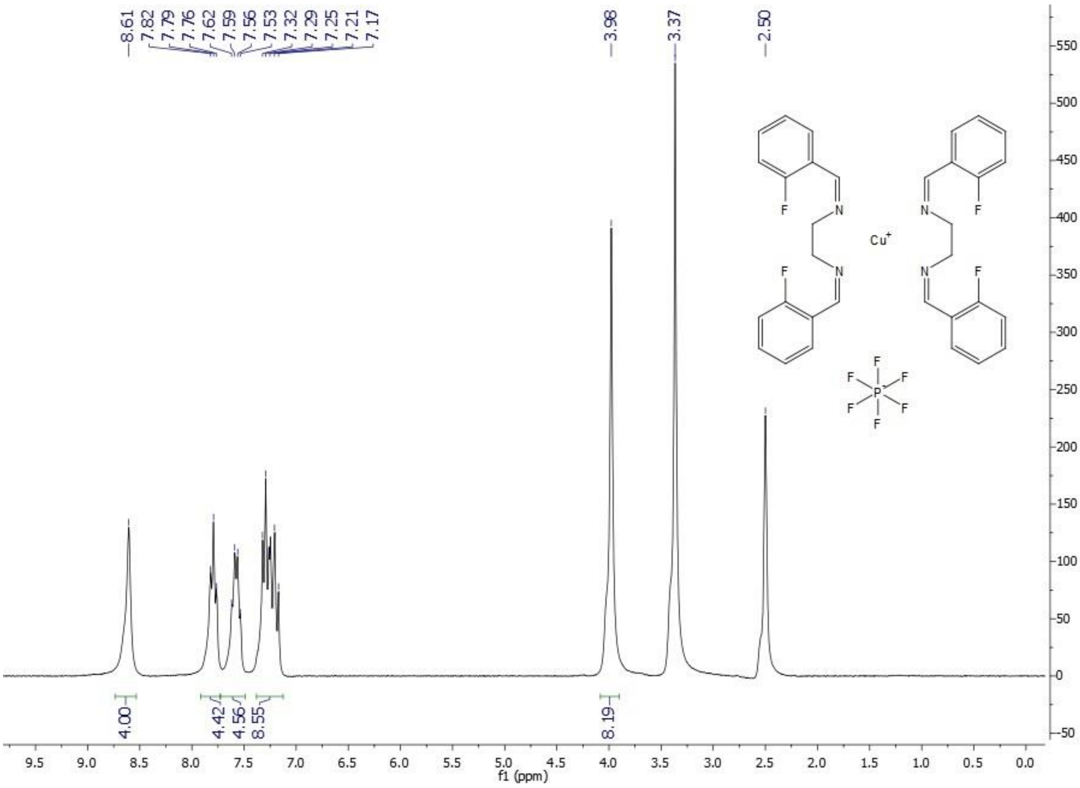


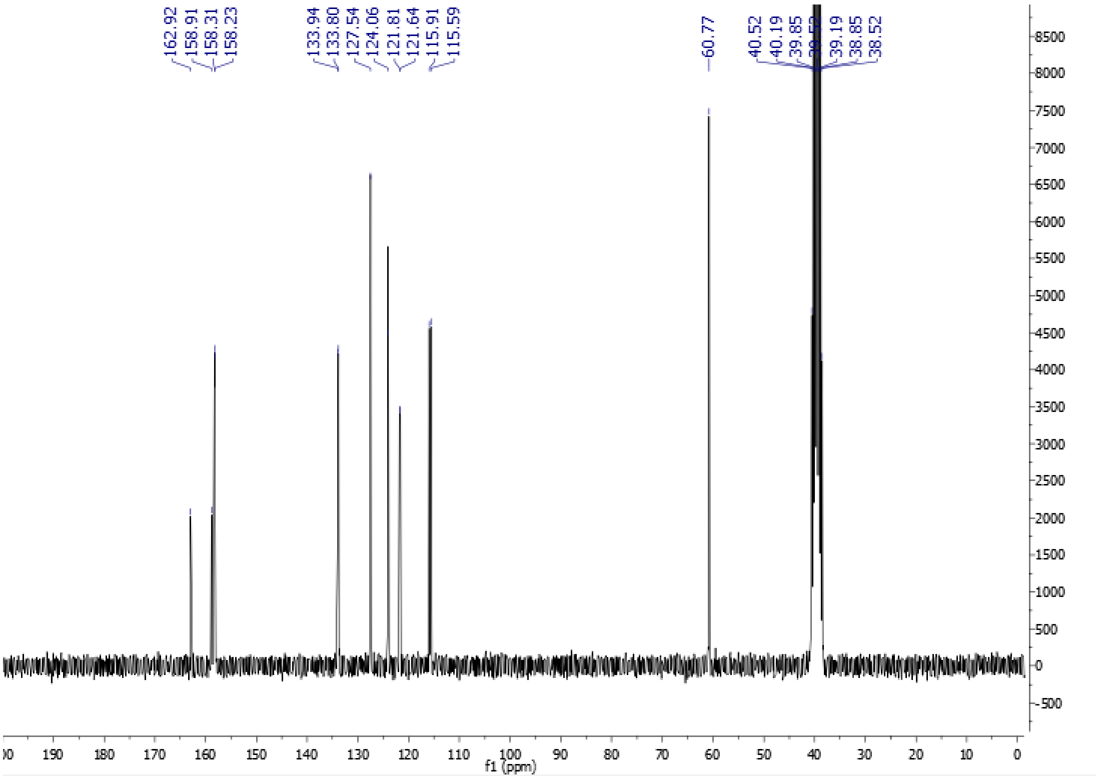
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)



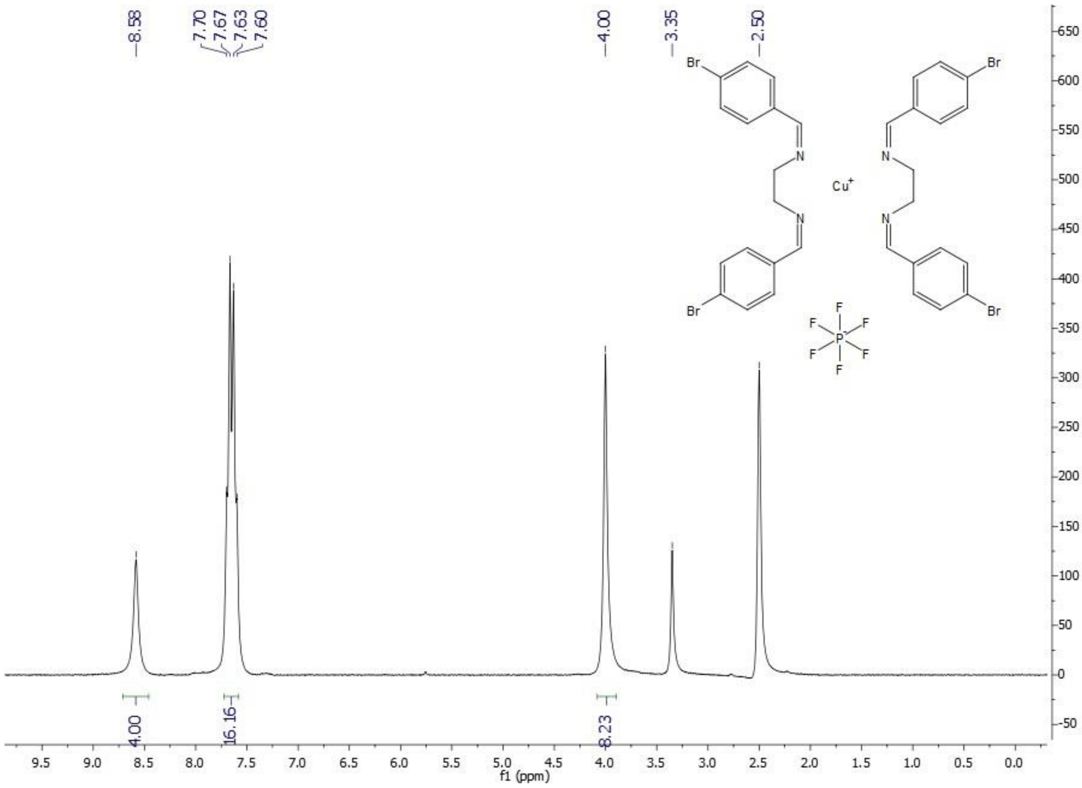
12
11
10
9
8
7
6
5
4
3
2
1
0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)

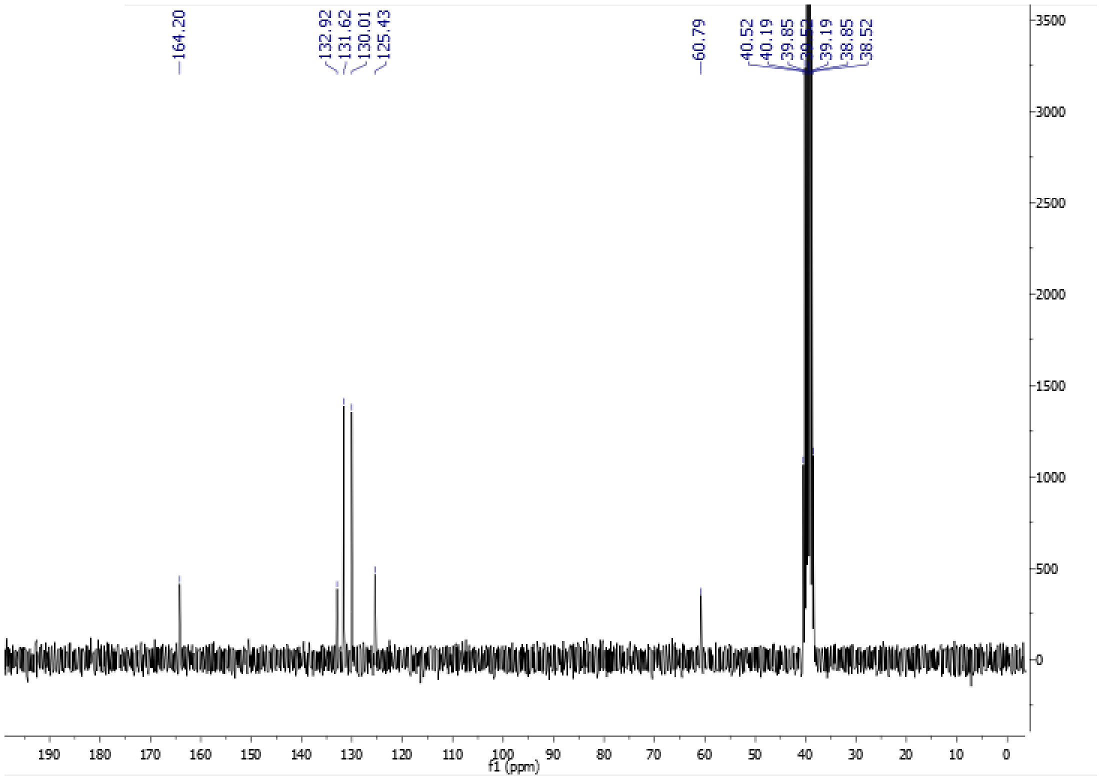
Compound **6k**


8.61
7.82
7.79
7.76
7.62
7.59
7.56
7.53
7.32
7.29
7.25
7.21
7.17
3.98
3.37
2.50
4.00
4.42
4.56
8.55
8.19
F
N
Cu+
F
F
P
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
f1 (ppm)
550
500
450
400
350
300
250
200
150
100
50
0
-50

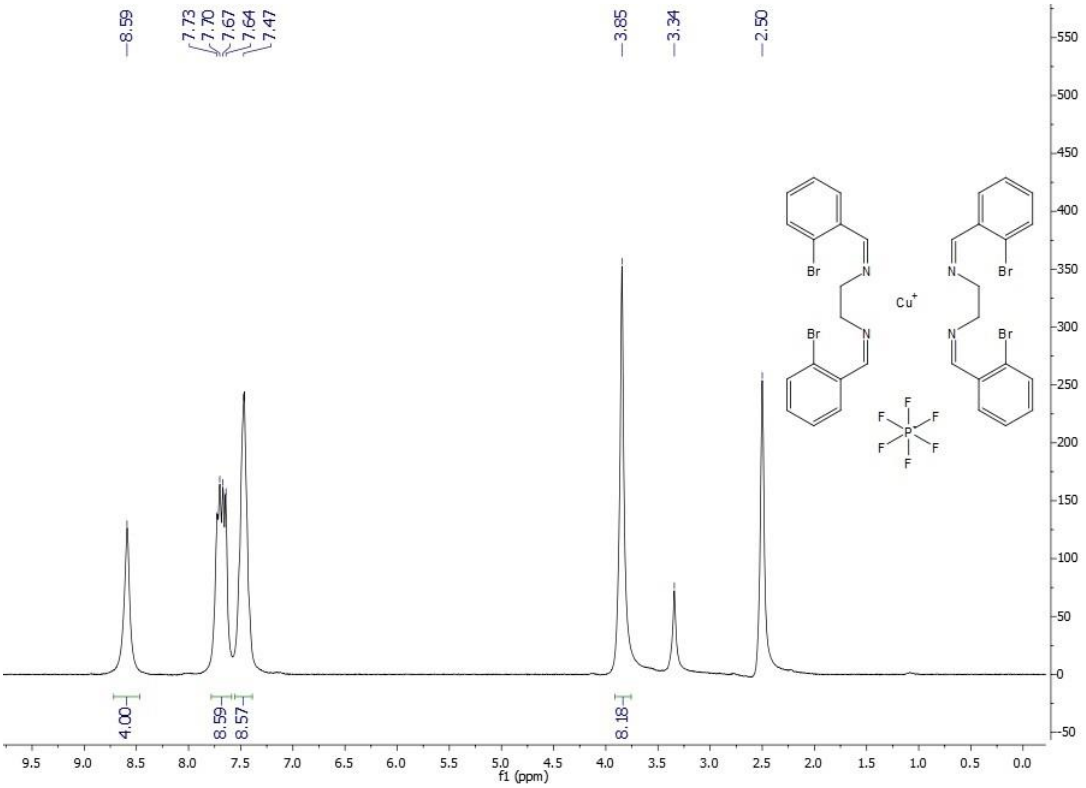

162.92
158.91
158.31
158.23
133.94
133.80
127.54
124.06
121.81
121.64
115.91
115.59
60.77
40.52
40.19
39.85
39.52
39.19
38.85
38.52
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

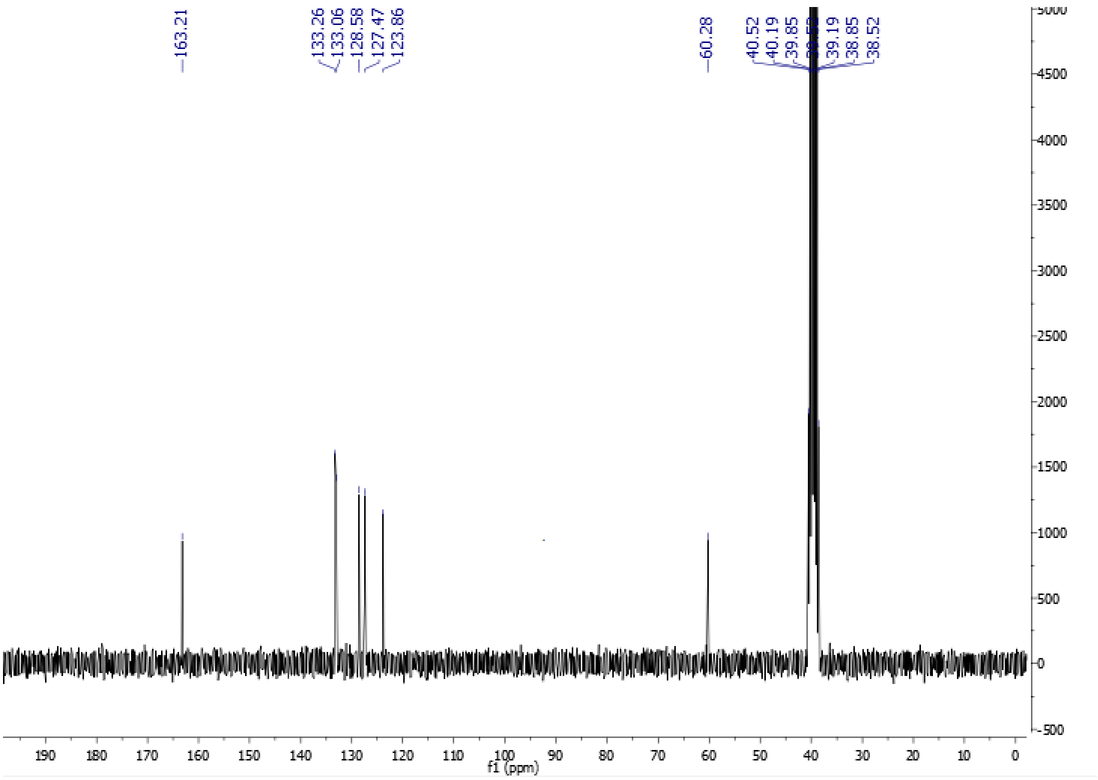
Compound **6l**


8.58
7.70
7.67
7.63
7.60
4.00
3.35
2.50
Br
Br
Br
Br
N
N
N
N
Cu+
F
F
F
F
F
F
P
4.00
16.16
8.23
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
f1 (ppm)
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

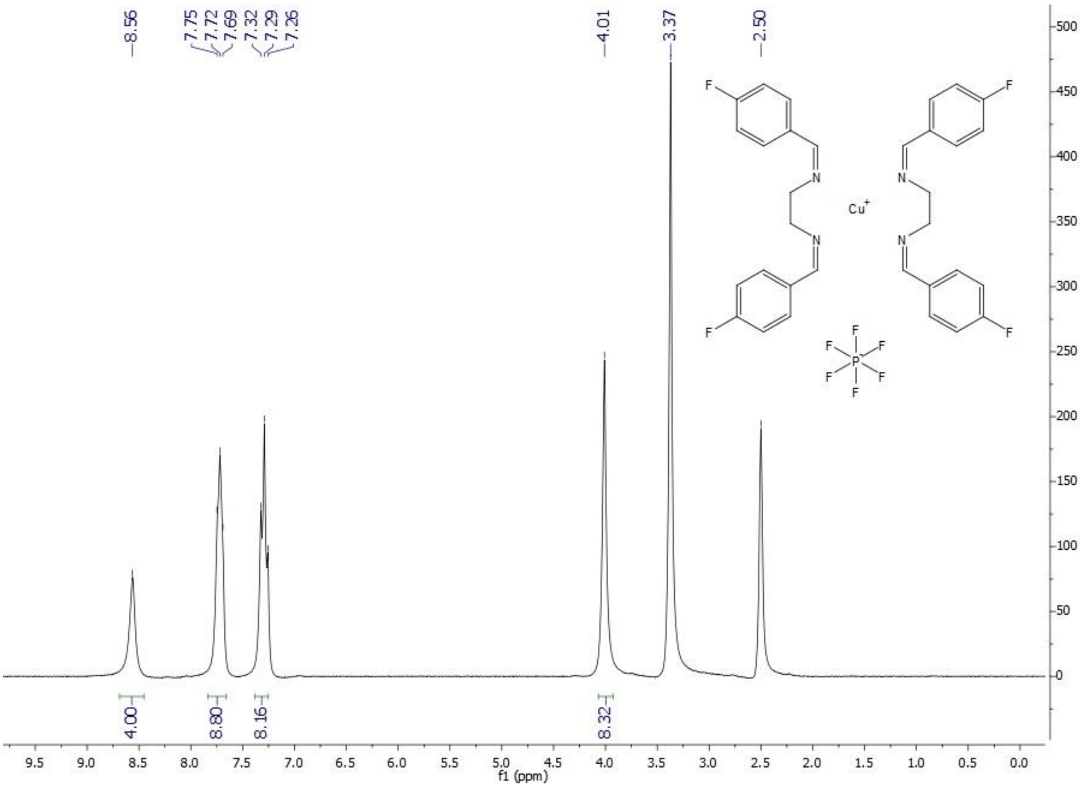

164.20
132.92
131.62
130.01
125.43
60.79
40.52
40.19
39.85
39.52
39.19
38.85
38.52
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
3500
3000
2500
2000
1500
1000
500
0

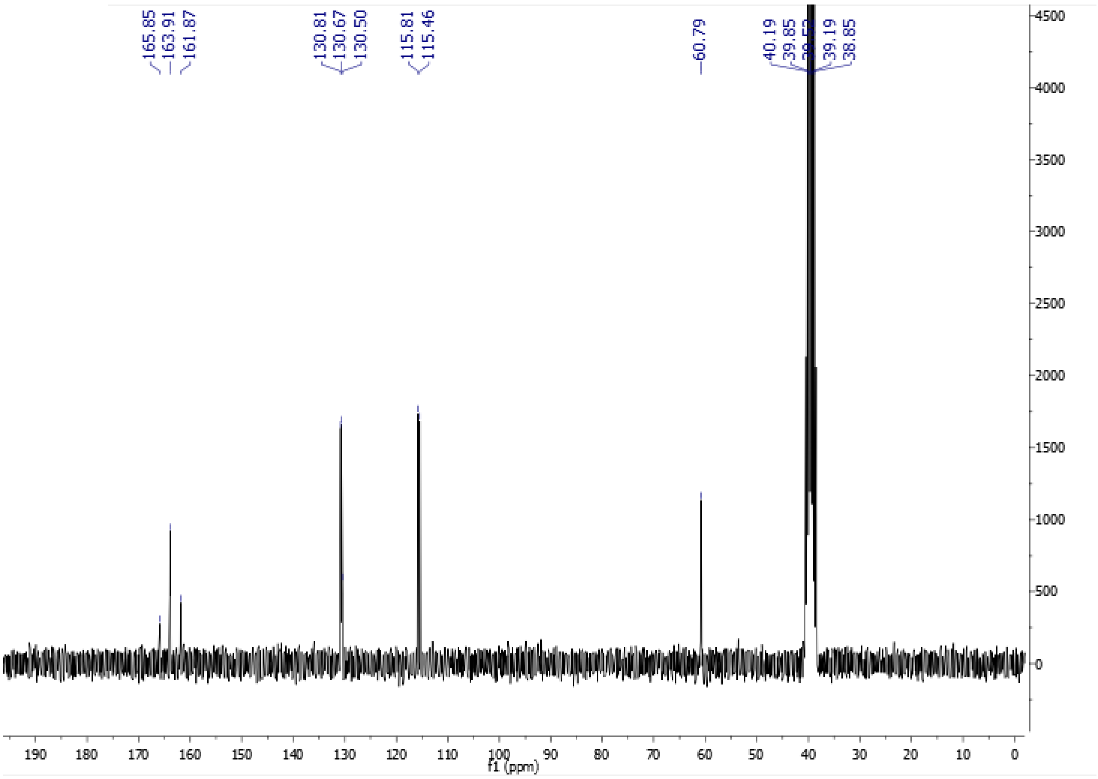
Compound **6m**


8.59
7.73
7.70
7.67
7.64
7.47
3.85
3.34
2.50
4.00
8.59
8.57
8.18
Br
N
Cu+
F
P
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
f1 (ppm)
550 500 450 400 350 300 250 200 150 100 50 0 -50

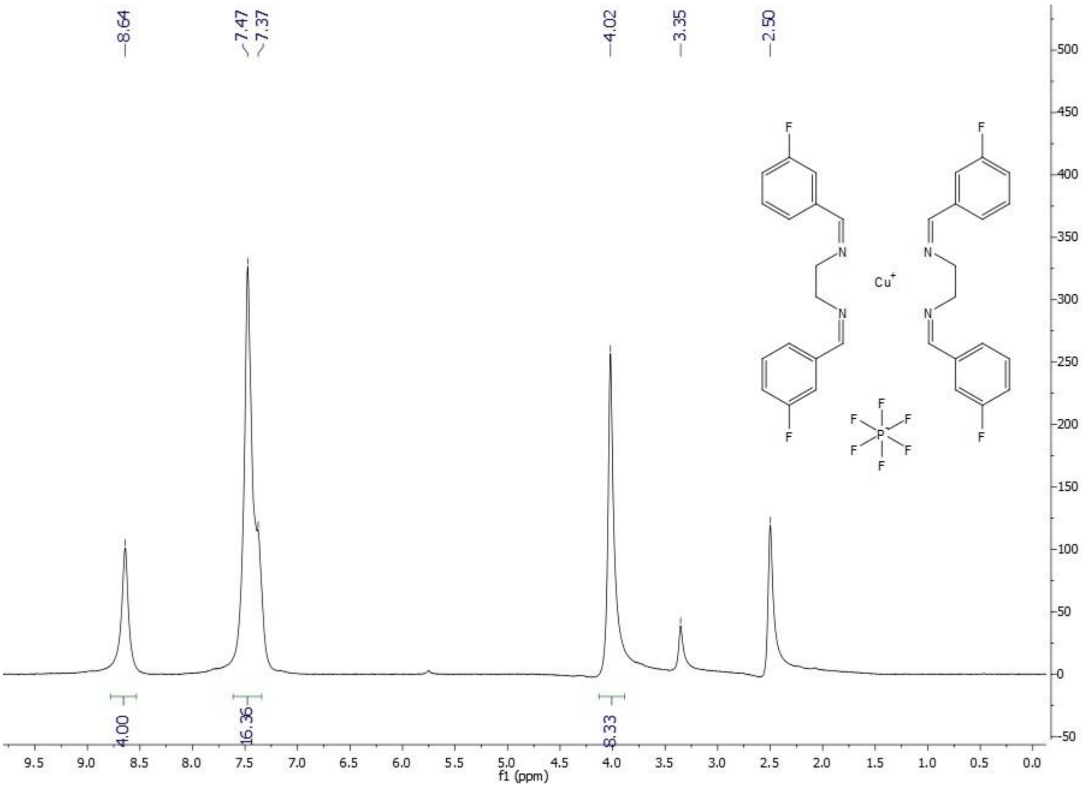

163.21
133.26
133.06
128.58
127.47
123.86
60.28
40.52
40.19
39.85
39.19
38.85
38.52
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

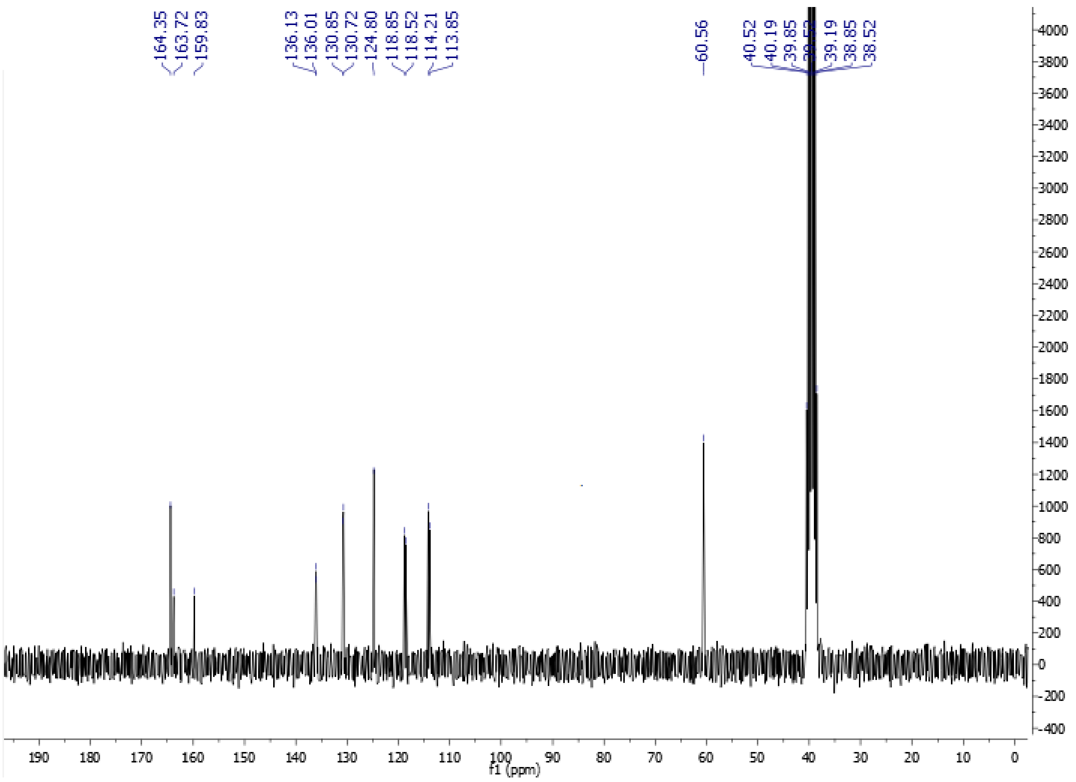
Compound **6n**


8.56
7.75
7.72
7.69
7.32
7.29
7.26
4.01
3.37
2.50
4.00
8.80
8.16
8.32
F
N
Cu+
P
f1 (ppm)

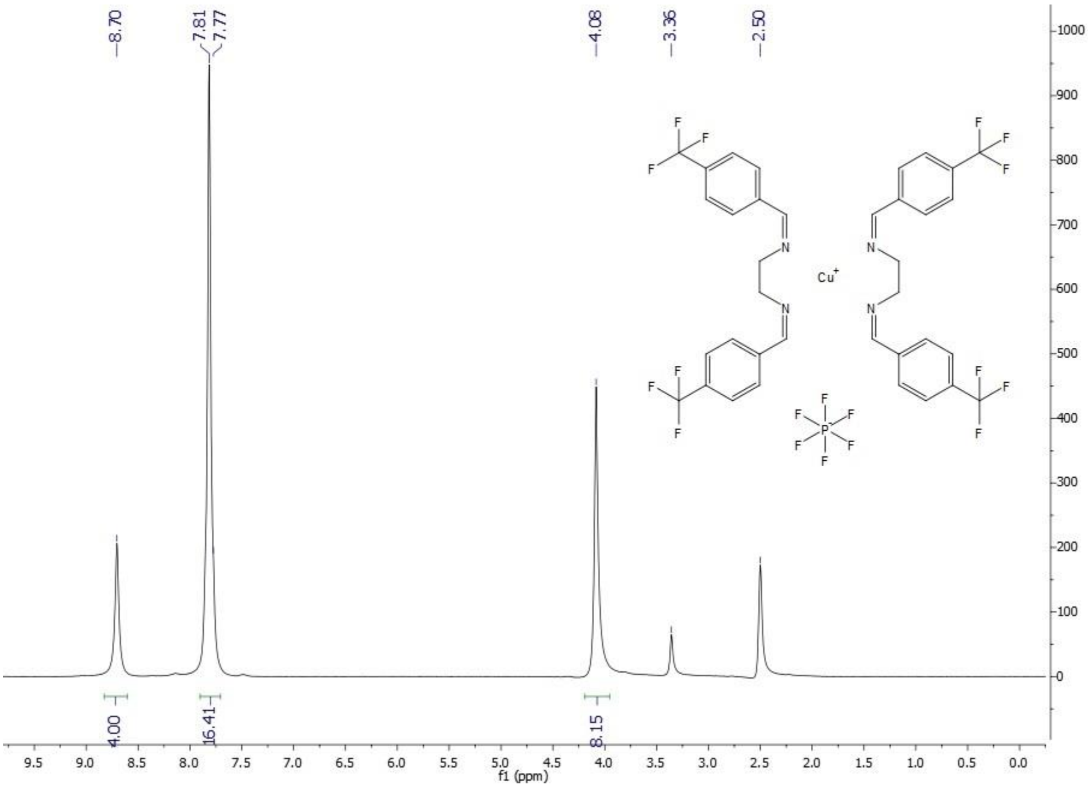

165.85
163.91
161.87
130.81
130.67
130.50
115.81
115.46
60.79
40.19
39.85
39.52
39.19
38.85
f1 (ppm)

Compound **6o**

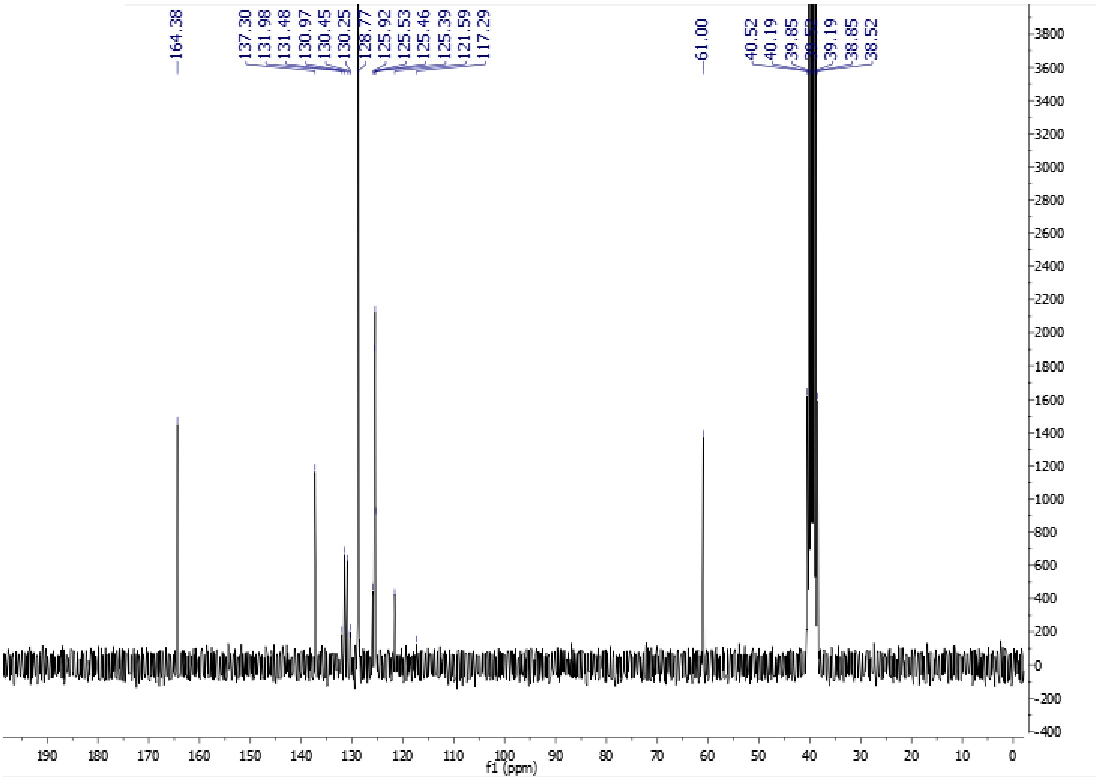

8.64
7.47
7.37
4.02
3.35
2.50
4.00
16.36
8.33
F
N
Cu+
P
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
500 450 400 350 300 250 200 150 100 50 0 -50


164.35
163.72
159.83
136.13
136.01
130.85
130.72
124.80
118.85
118.52
114.21
113.85
60.56
40.52
40.19
39.85
39.19
38.85
38.52
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200 -400

Compound **6p**

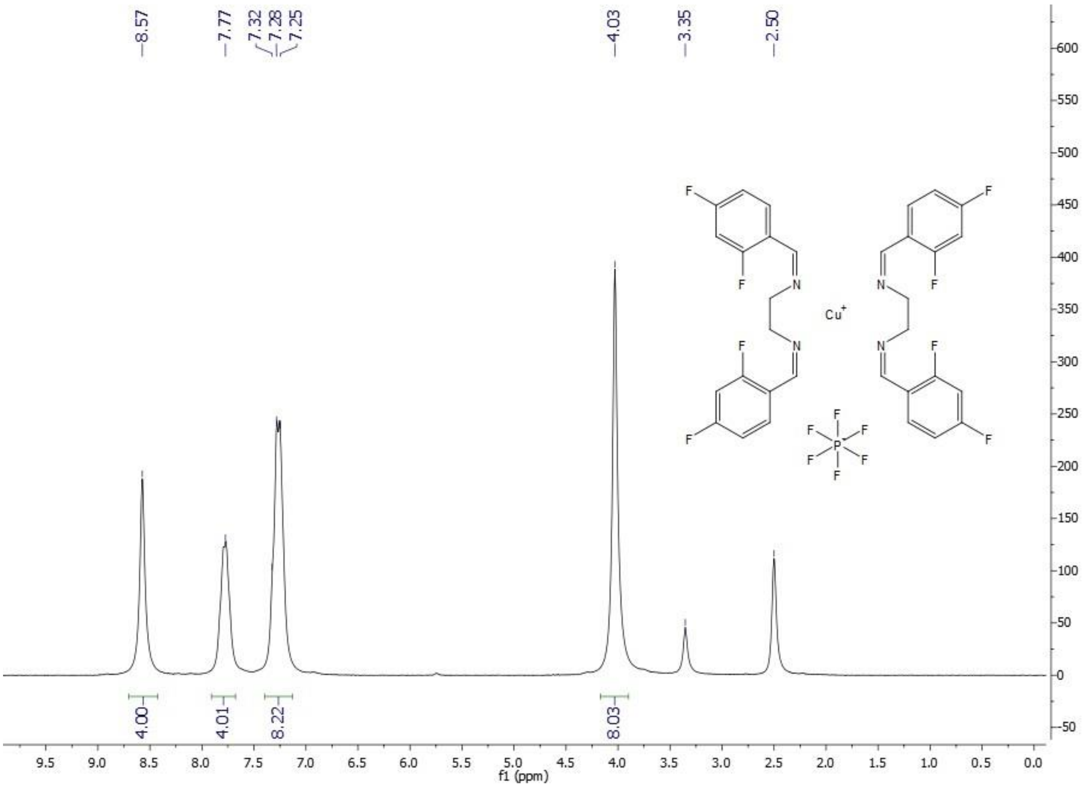


8.70
7.81
7.77
4.08
3.36
2.50
4.00
16.41
8.15
F
F
F
N
N
N
N
Cu+
P
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1000
900
800
700
600
500
400
300
200
100
0

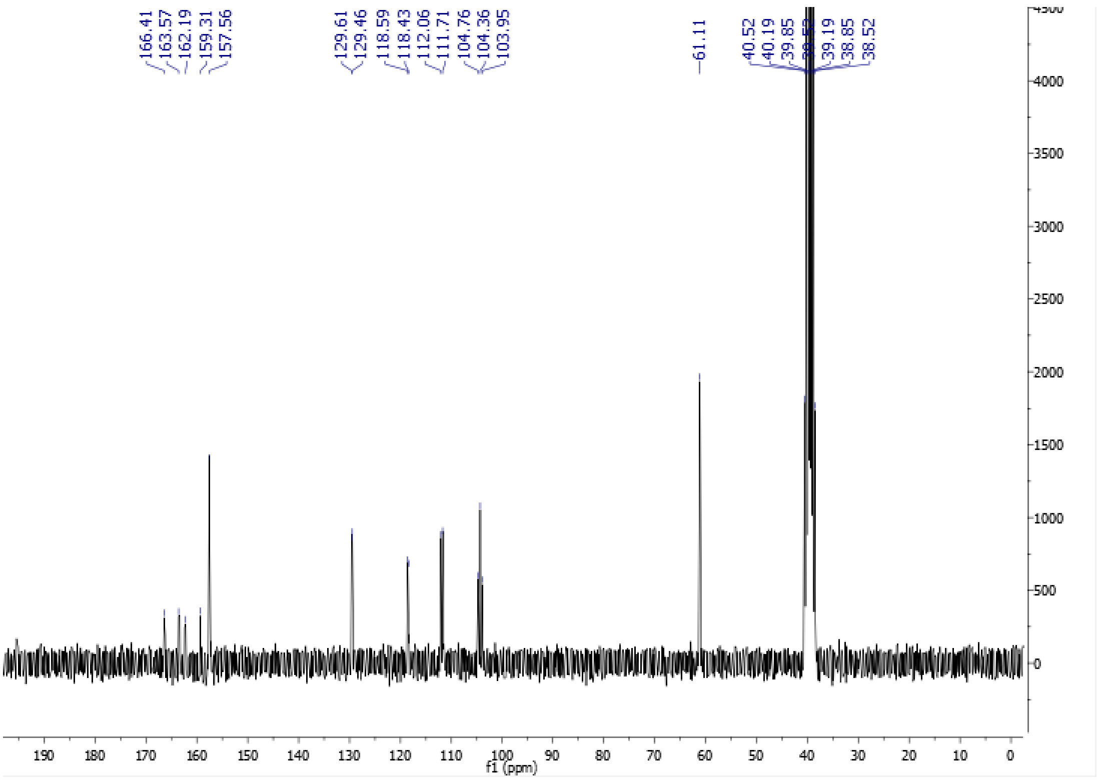


164.38
137.30
131.98
131.48
130.97
130.45
130.25
128.77
125.92
125.53
125.46
125.39
121.59
117.29
61.00
40.52
40.19
39.85
39.52
39.19
38.85
38.52
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400

Compound **6q**

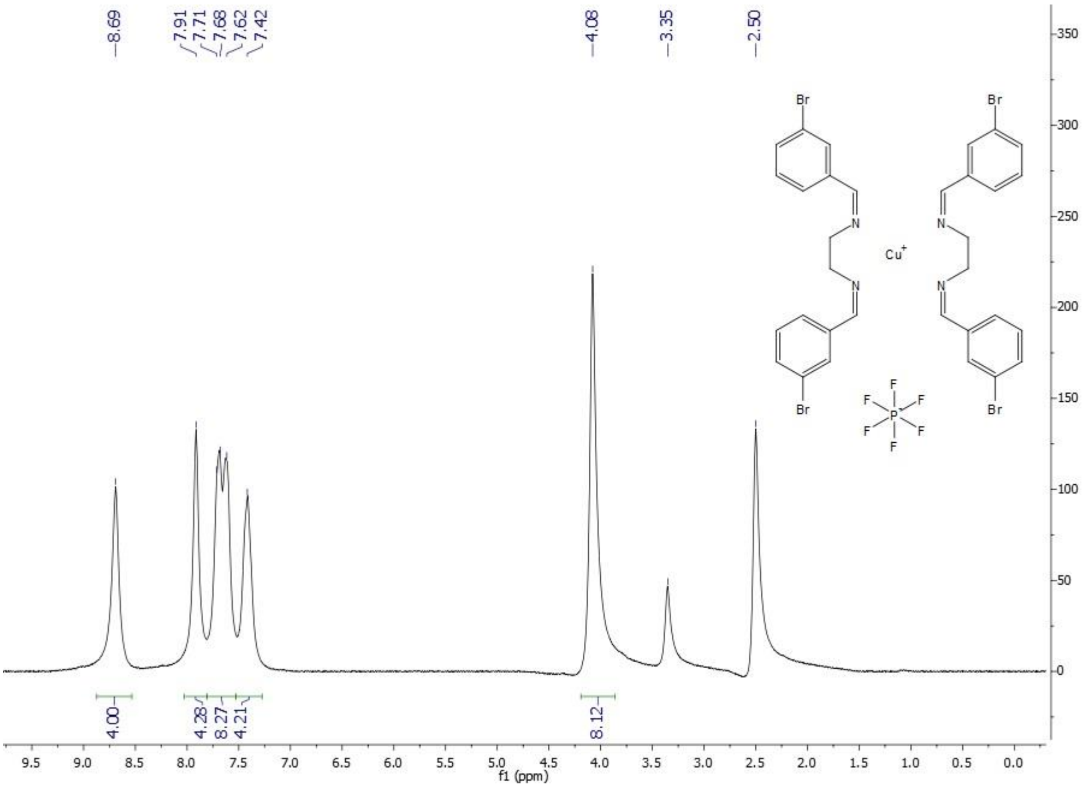


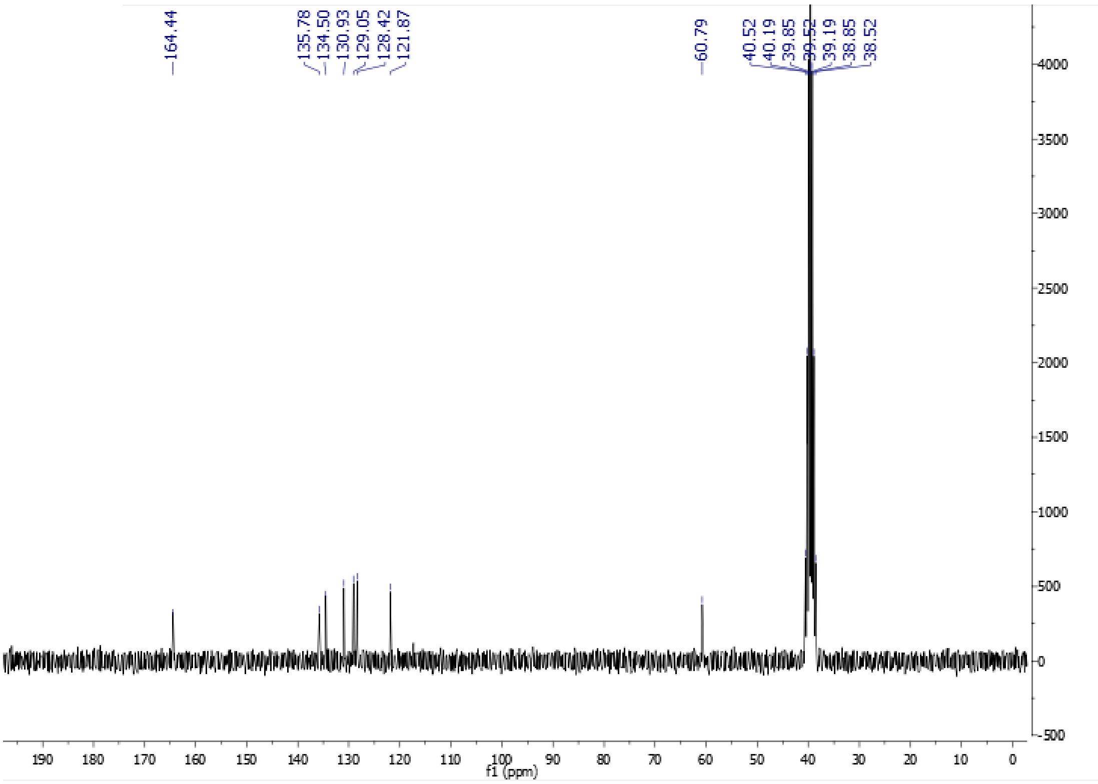
8.57
7.77
7.32
7.28
7.25
4.03
3.35
2.50
4.00
4.01
8.22
8.03
F
N
Cu+
P
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



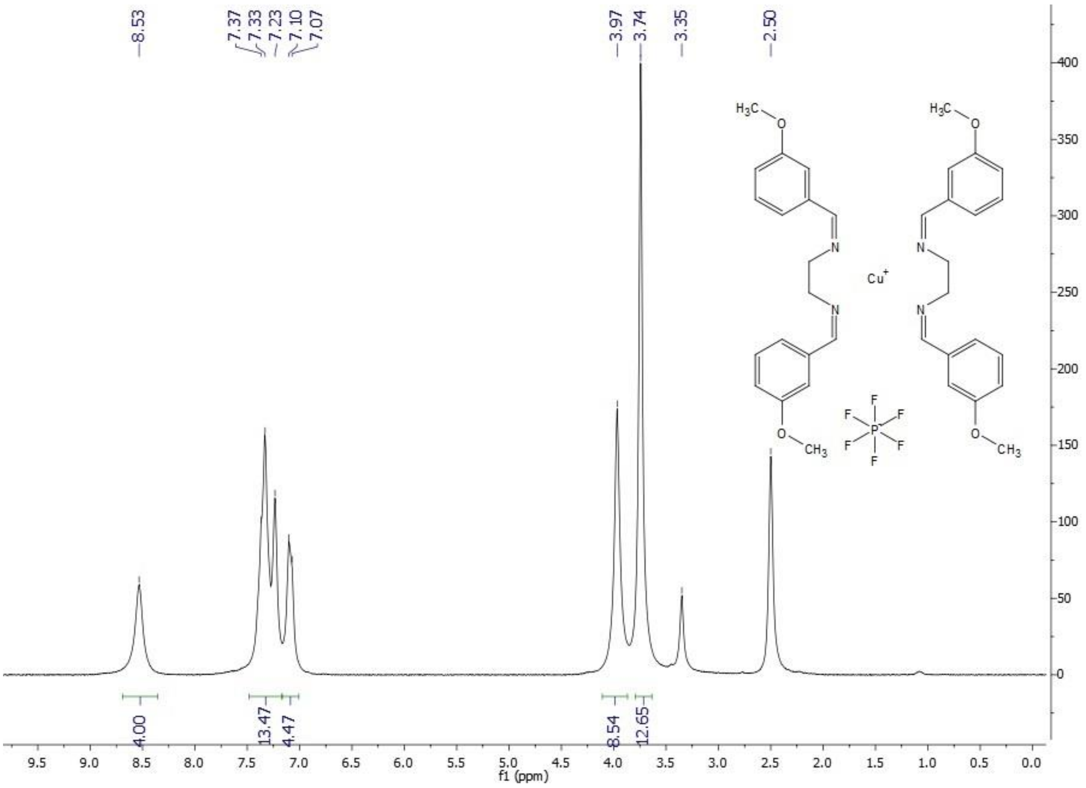
166.41
163.57
162.19
159.31
157.56
129.61
129.46
118.59
118.43
112.06
111.71
104.76
104.36
103.95
61.11
40.52
40.19
39.85
39.52
39.19
38.85
38.52
4500
4000
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

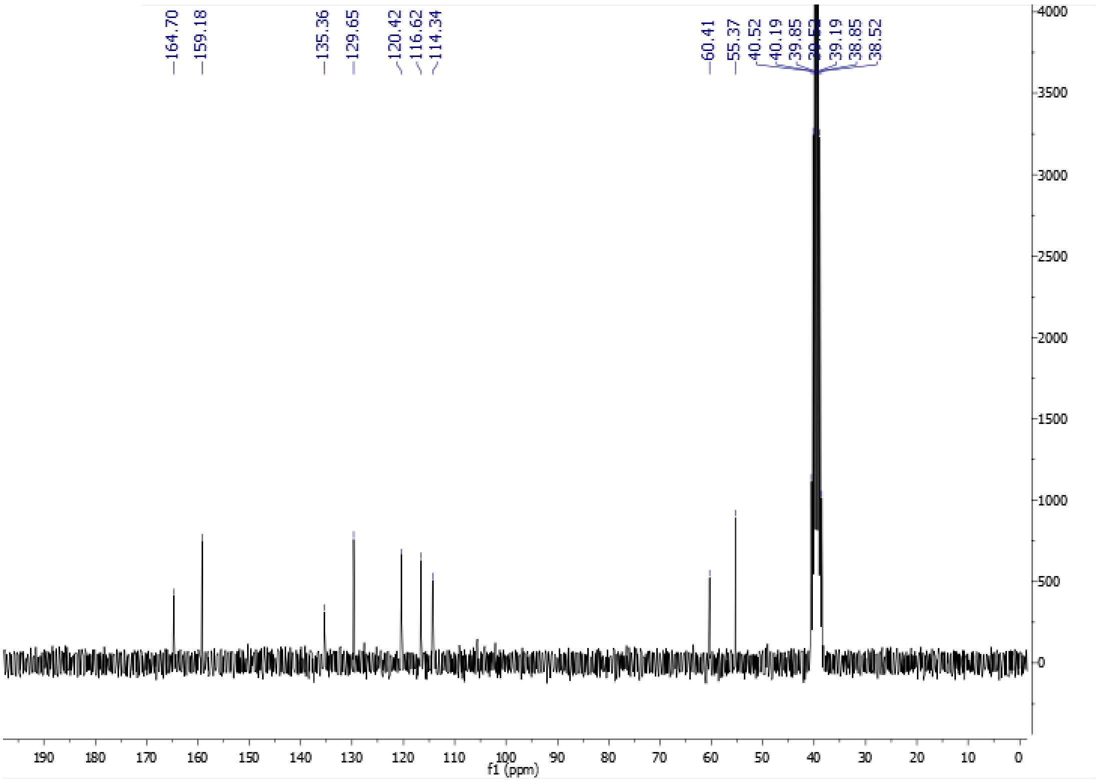
Compound **6r**


8.69
7.91
7.71
7.68
7.62
7.42
4.08
3.35
2.50
Br
Br
Br
Br
N
N
N
N
Cu+
F
F
F
F
F
F
P
4.00
4.28
8.27
4.21
8.12
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
f1 (ppm)
350
300
250
200
150
100
50
0

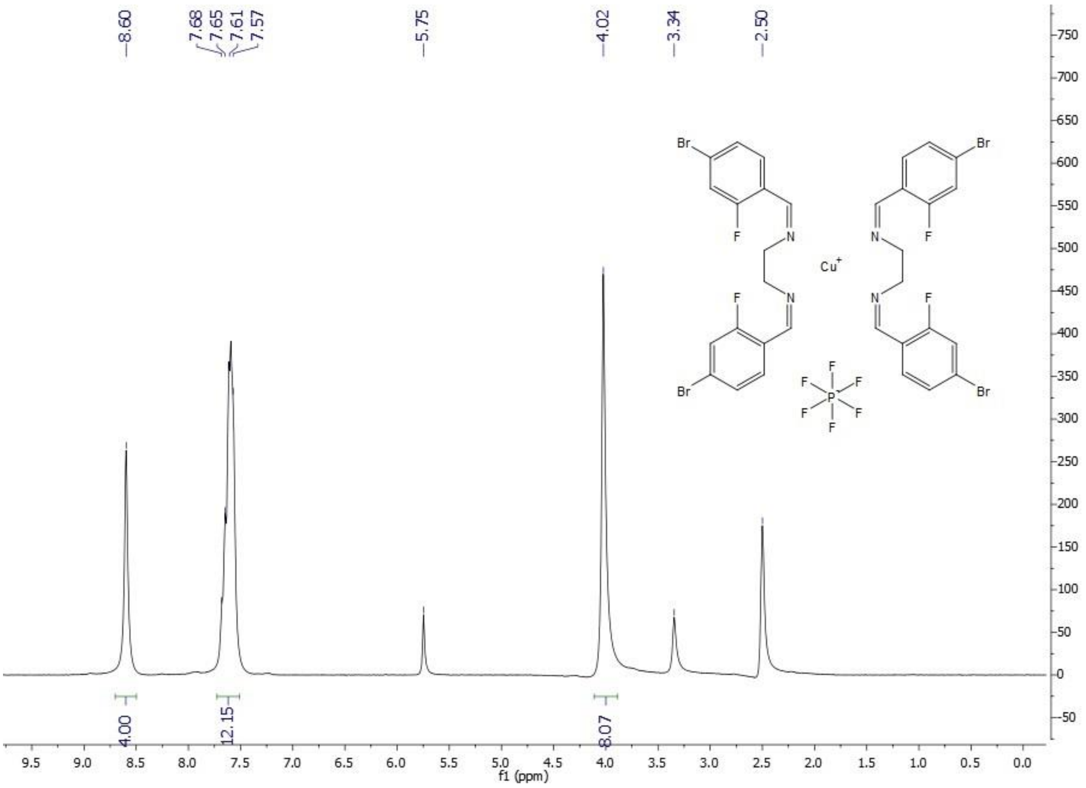

164.44
135.78
134.50
130.93
129.05
128.42
121.87
60.79
40.52
40.19
39.85
39.52
39.19
38.85
38.52
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0
-500

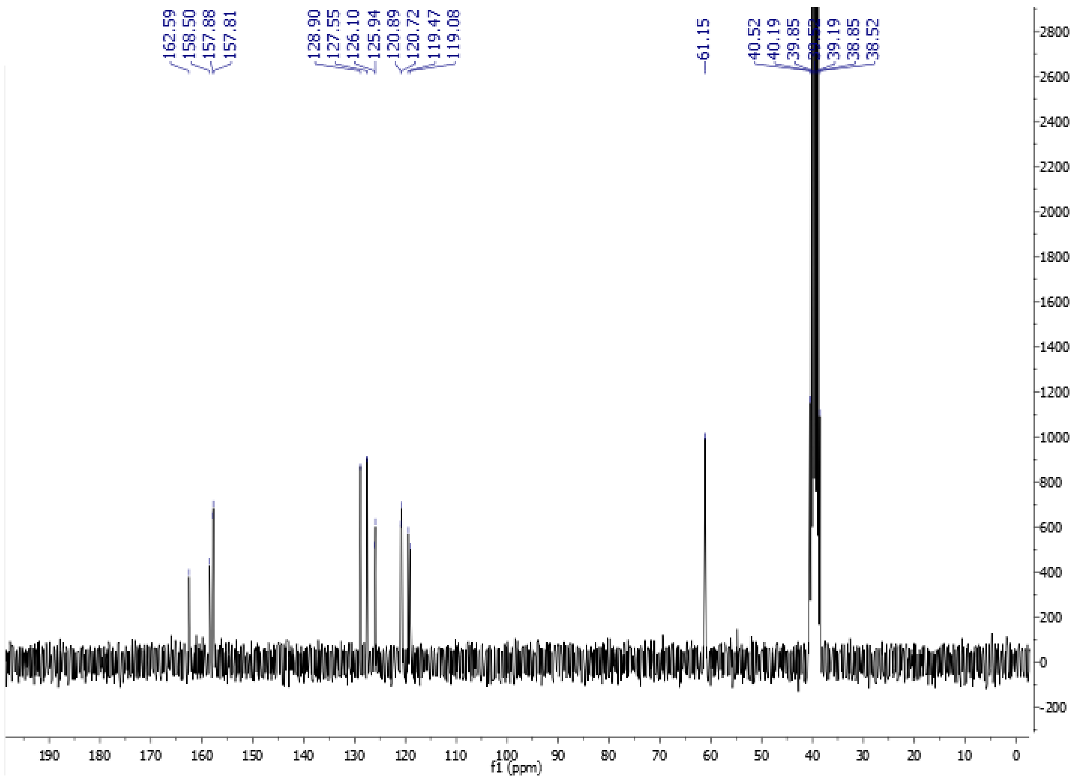
Compound **6s**


8.53
7.37
7.33
7.23
7.10
7.07
3.97
3.74
3.35
2.50
4.00
13.47
4.47
8.54
12.65
f1 (ppm)
H$_3$C
O
N
Cu$^+$
F
P
CH$_3$

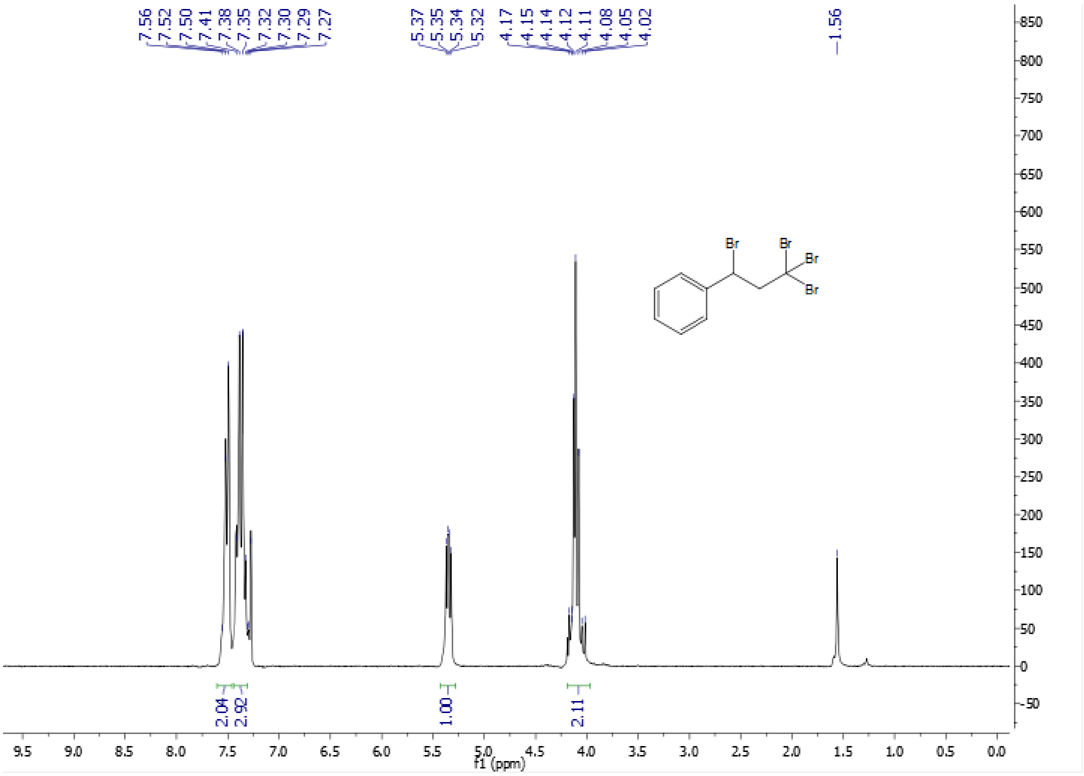

164.70
159.18
135.36
129.65
120.42
116.62
114.34
60.41
55.37
40.52
40.19
39.85
39.19
38.85
38.52
f1 (ppm)

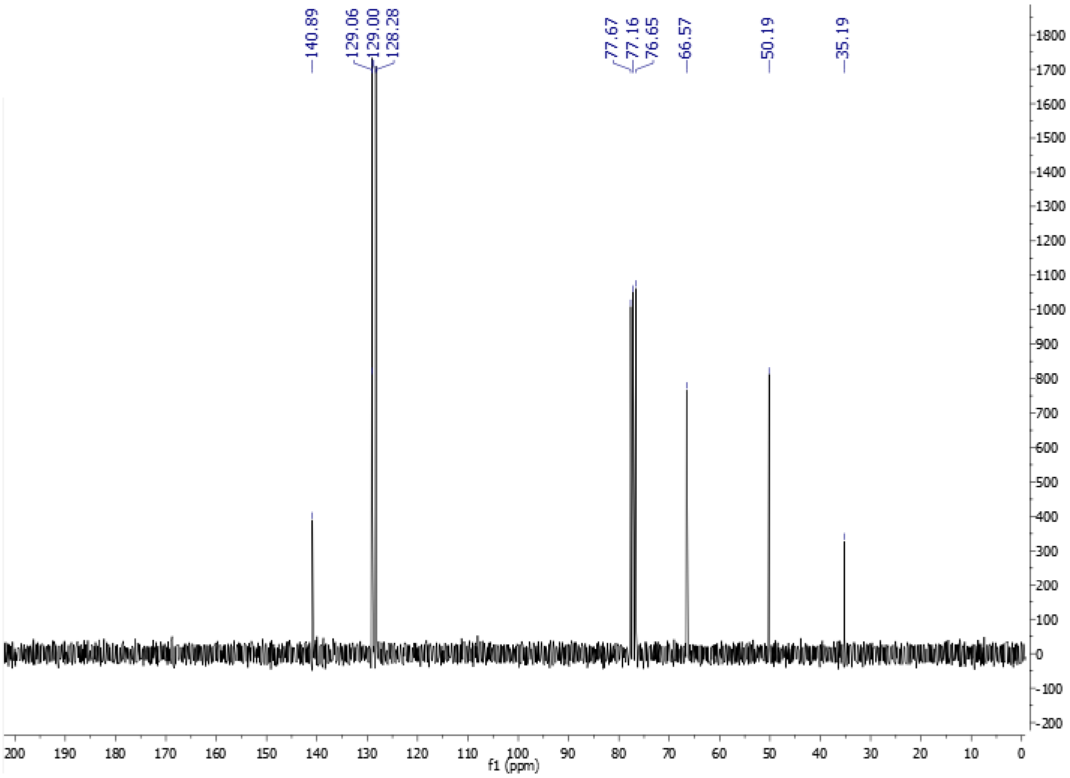
Compound **6t**


8.60
7.68
7.65
7.61
7.57
5.75
4.02
3.34
2.50
Br
F
N
Cu+
F
P
4.00
12.15
8.07
f1 (ppm)

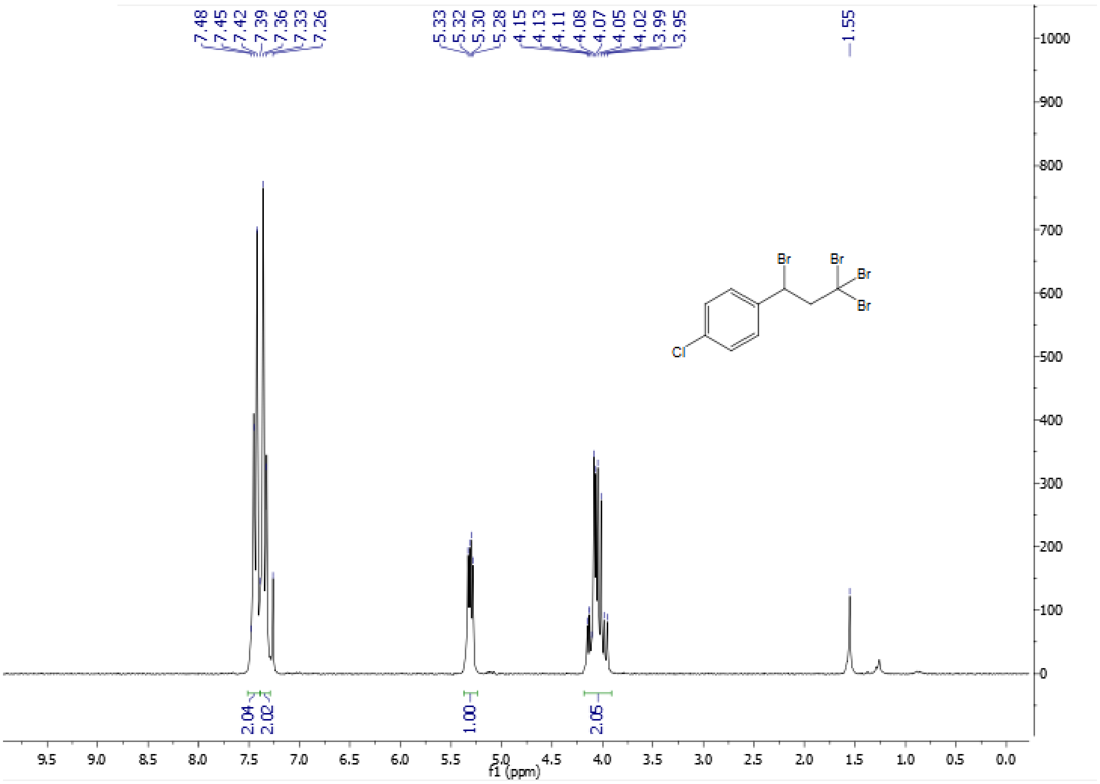

162.59
158.50
157.88
157.81
128.90
127.55
126.10
125.94
120.89
120.72
119.47
119.08
61.15
40.52
40.19
39.85
39.19
38.85
38.52
f1 (ppm)

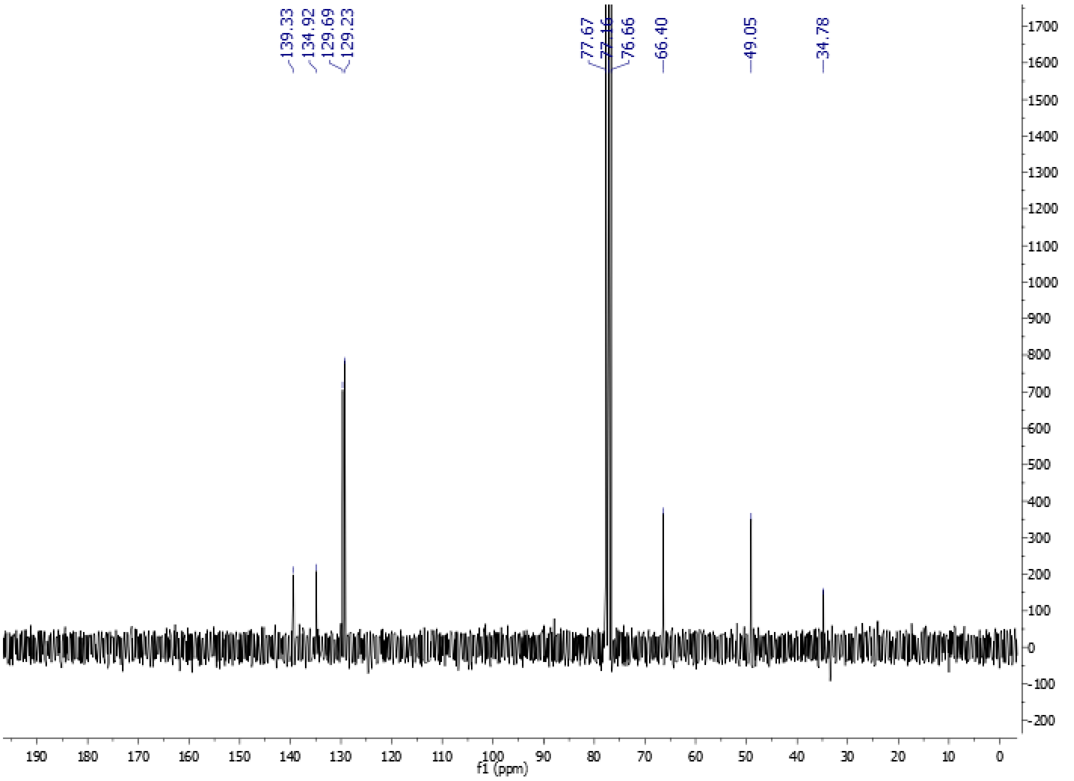
Compound **9a**


7.56
7.52
7.50
7.41
7.38
7.35
7.32
7.30
7.29
7.27
5.37
5.35
5.34
5.32
4.17
4.15
4.14
4.12
4.11
4.08
4.05
4.02
1.56
Br
Br
Br
Br
2.04
2.92
1.00
2.11
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
f1 (ppm)
850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50

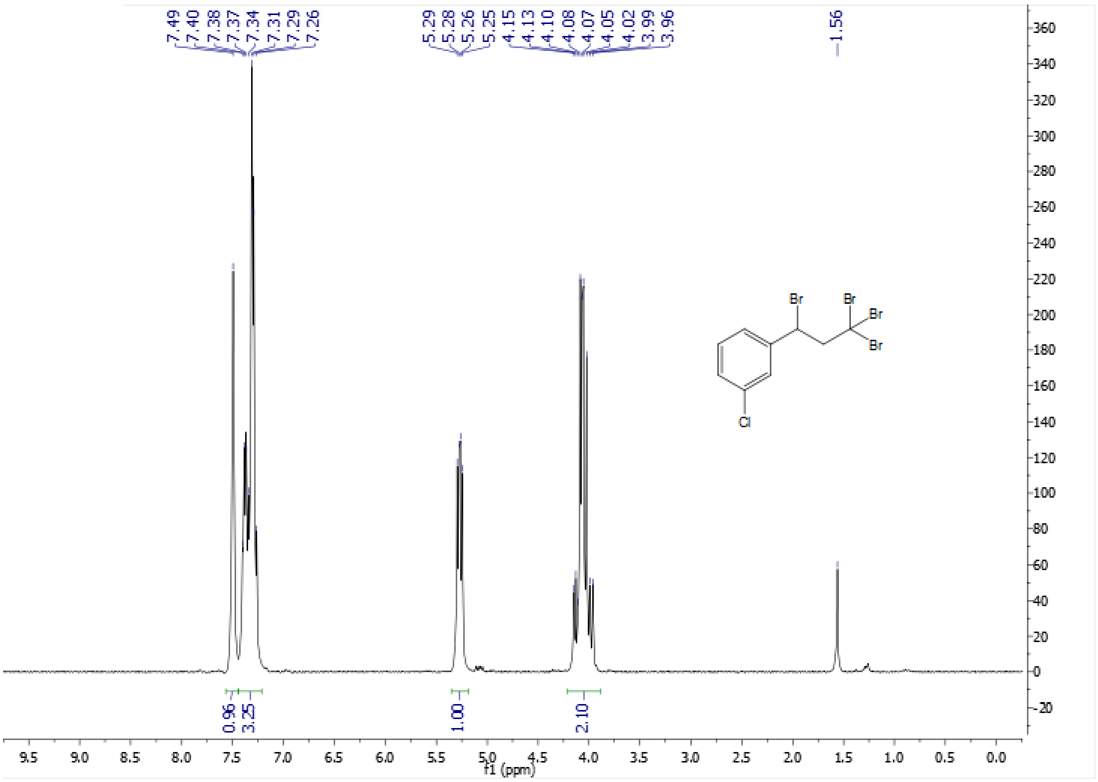

140.89
129.06
129.00
128.28
77.67
77.16
76.65
66.57
50.19
35.19
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200

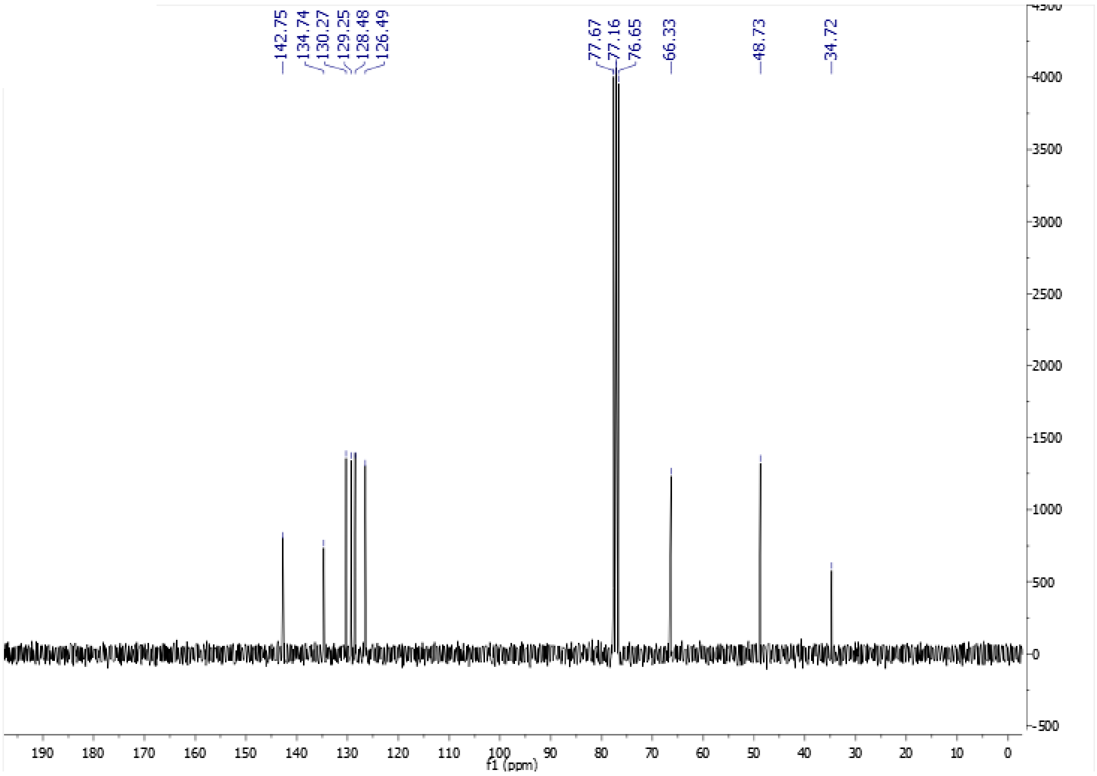
Compound **9b**


7.48
7.45
7.42
7.39
7.36
7.33
7.26
5.33
5.32
5.30
5.28
4.15
4.13
4.11
4.08
4.07
4.05
4.02
3.99
3.95
1.55
Br
Br
Br
Br
Cl
2.04
2.02
1.00
2.05
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
f1 (ppm)
1000
900
800
700
600
500
400
300
200
100
0

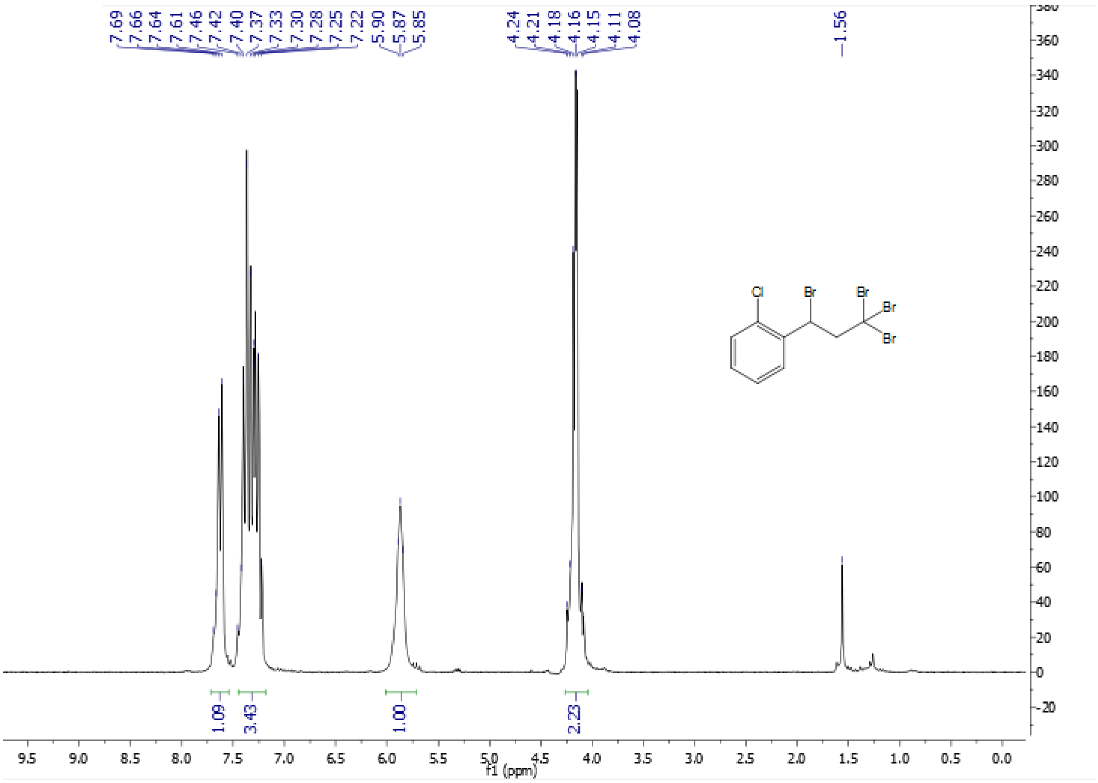

139.33
134.92
129.69
129.23
77.67
77.16
76.66
66.40
49.05
34.78
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200

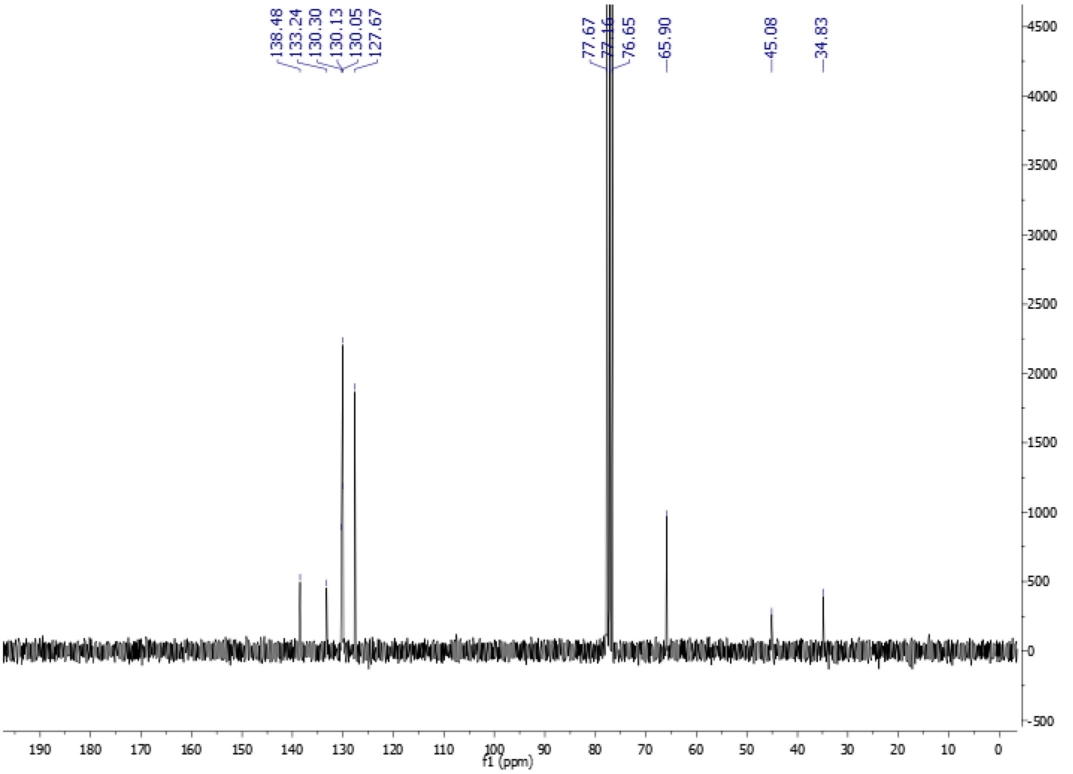
Compound **9c**


7.49
7.40
7.38
7.37
7.34
7.31
7.29
7.26
5.29
5.28
5.26
5.25
4.15
4.13
4.10
4.08
4.07
4.05
4.02
3.99
3.96
1.56
Br
Br
Br
Br
Cl
0.96
3.25
1.00
2.10
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
f1 (ppm)
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

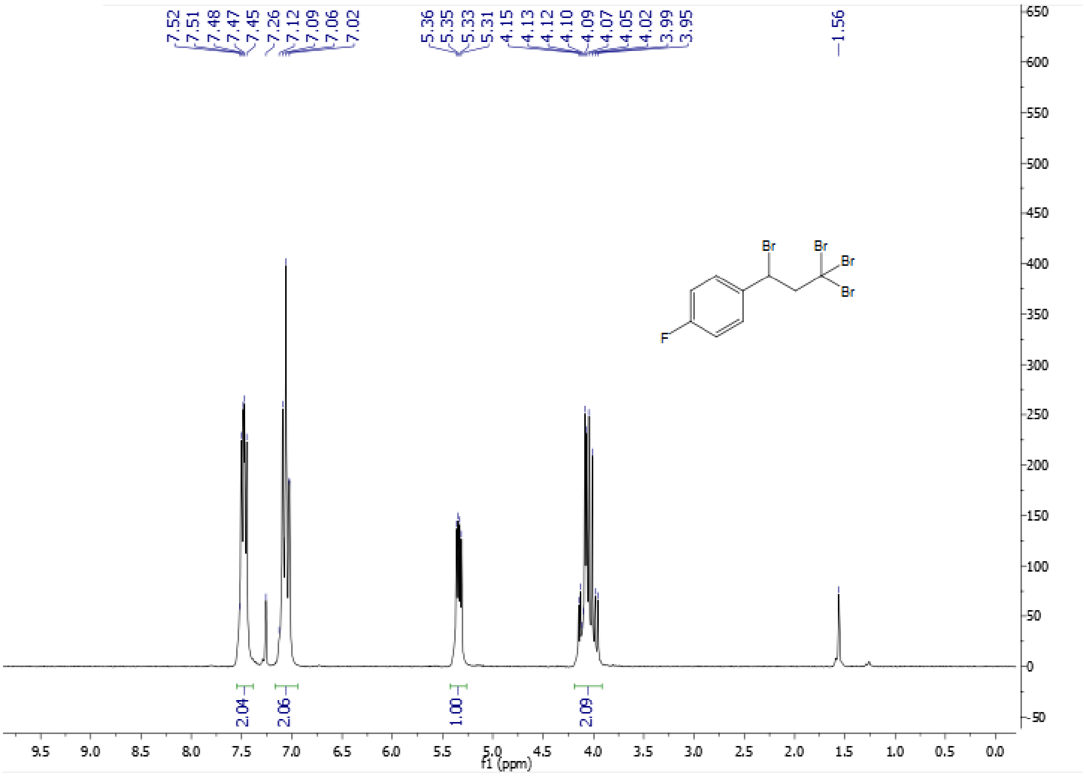

142.75
134.74
130.27
129.25
128.48
126.49
77.67
77.16
76.65
66.33
48.73
34.72
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

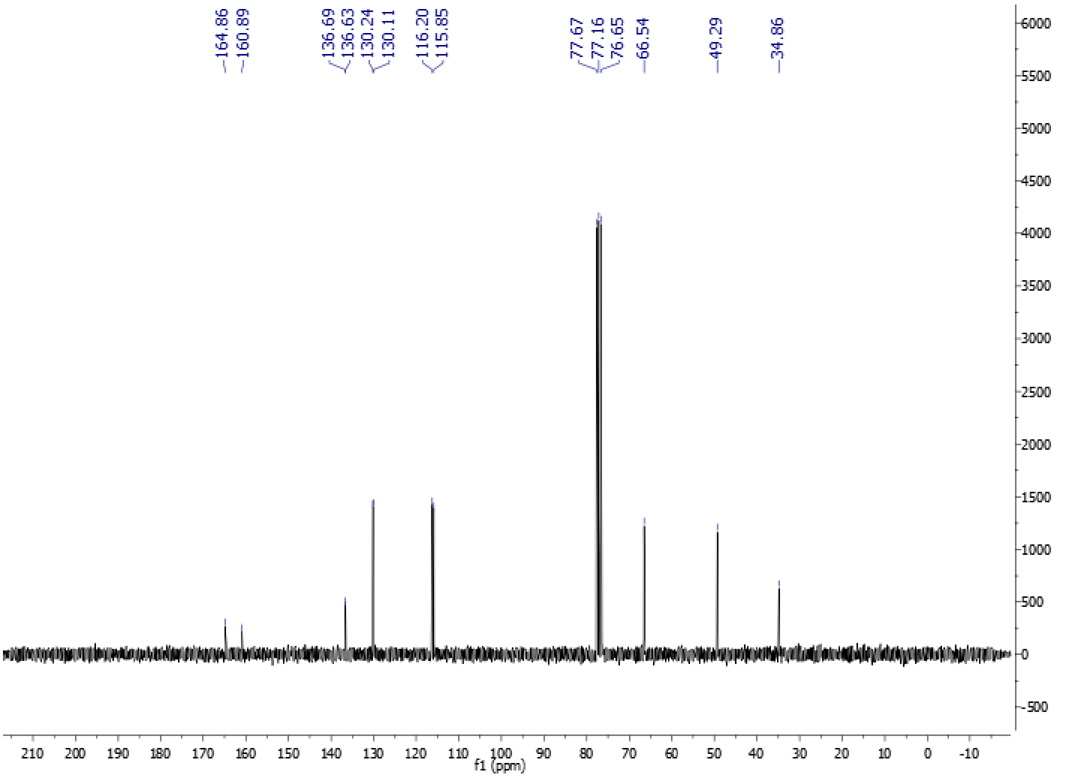
Compound **9d**


7.69
7.66
7.64
7.61
7.46
7.42
7.40
7.37
7.33
7.30
7.28
7.25
7.22
5.90
5.87
5.85
4.24
4.21
4.18
4.16
4.15
4.11
4.08
1.56
Cl
Br
Br
Br
Br
1.09
3.43
1.00
2.23
f1 (ppm)

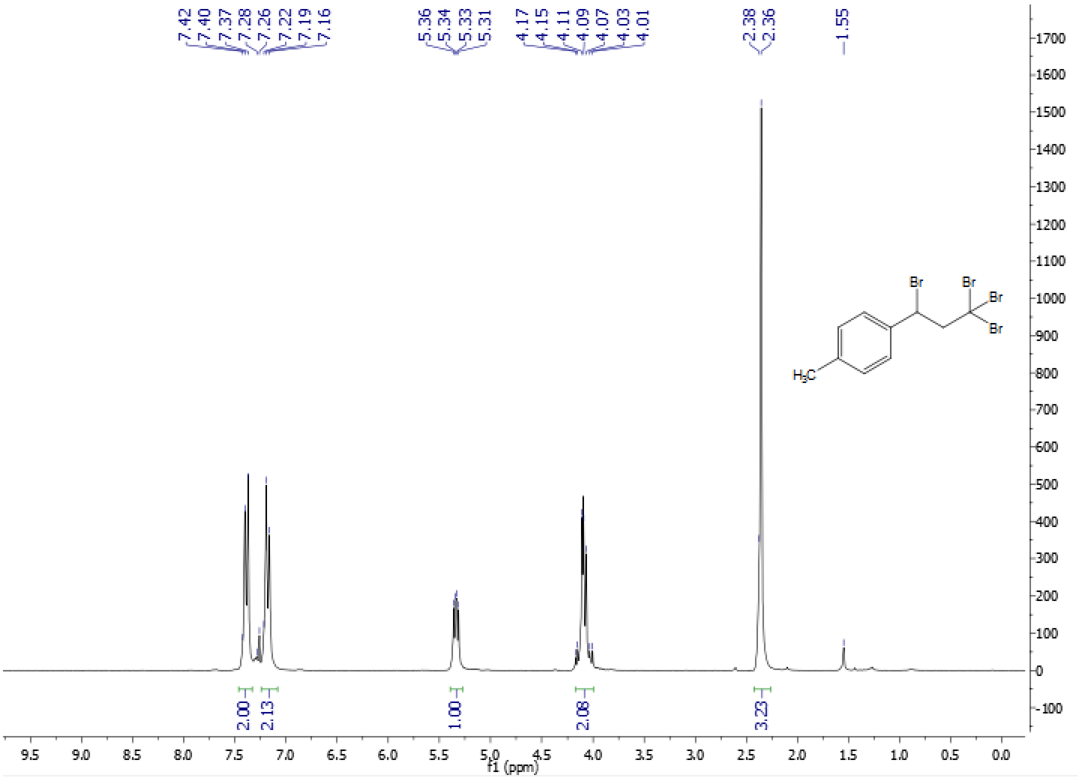

138.48
133.24
130.30
130.13
130.05
127.67
77.67
77.16
76.65
65.90
45.08
34.83
f1 (ppm)

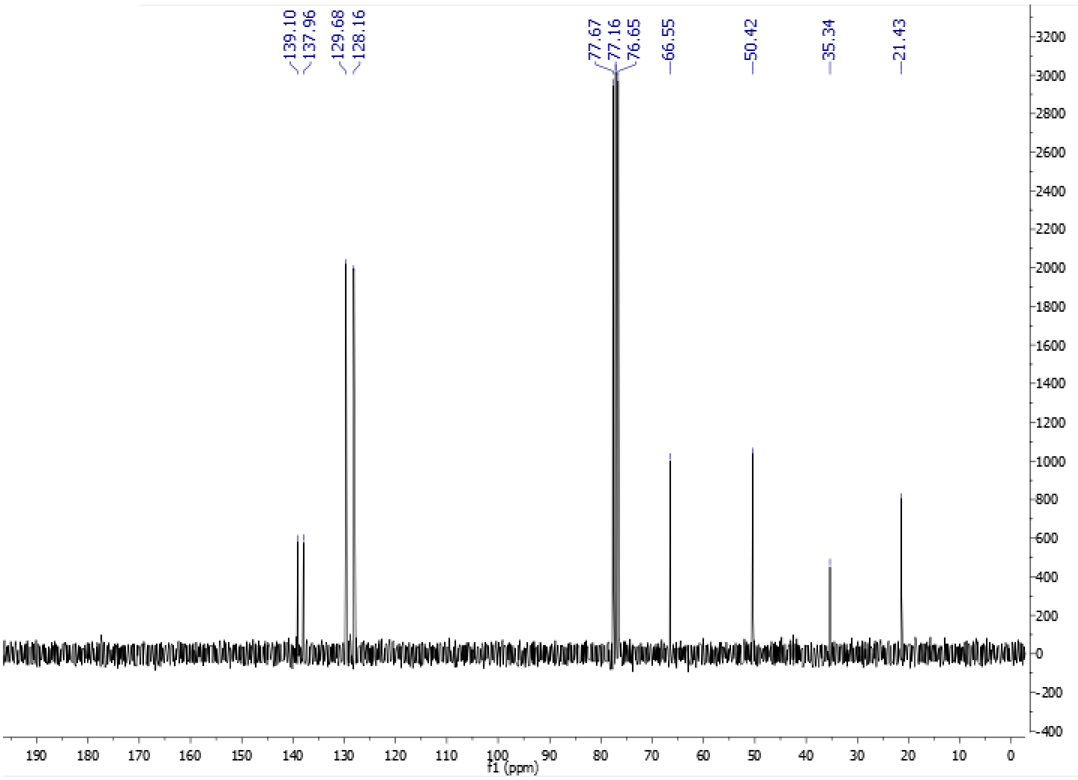
Compound **9e**


7.52
7.51
7.48
7.47
7.45
7.26
7.12
7.09
7.06
7.02
5.36
5.35
5.33
5.31
4.15
4.13
4.12
4.10
4.09
4.07
4.05
4.02
3.99
3.95
1.56
Br
Br
Br
Br
F
2.04
2.06
1.00
2.09
f1 (ppm)

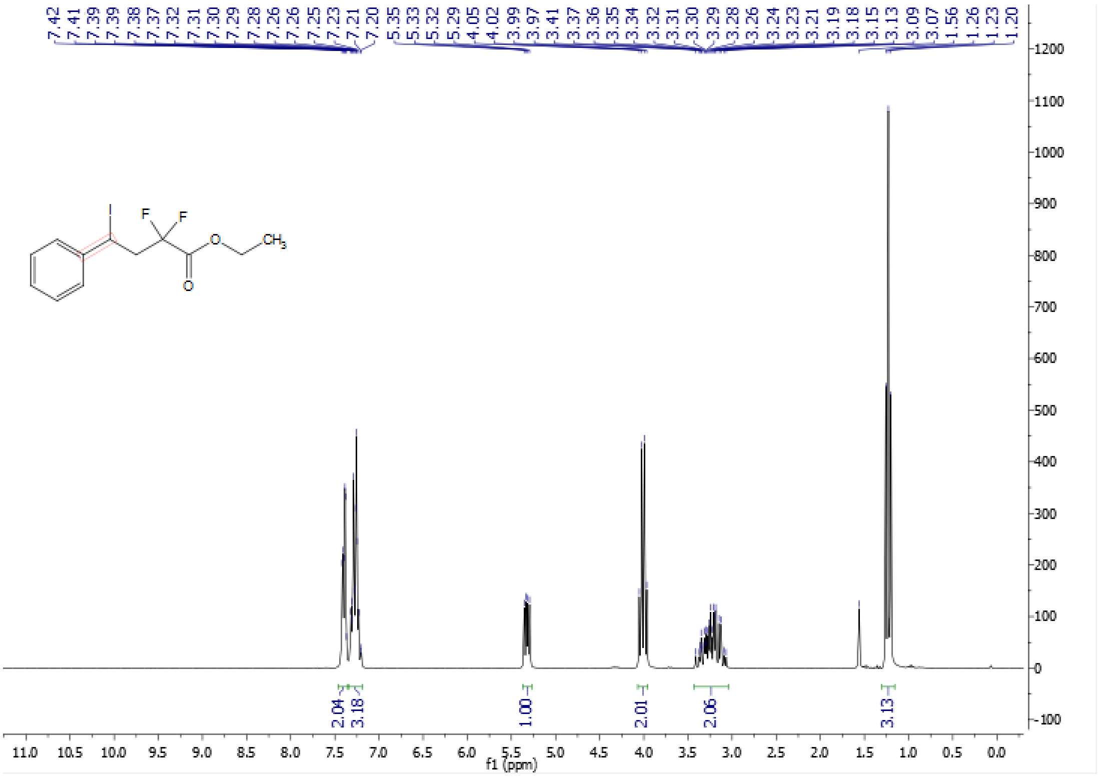

164.86
160.89
136.69
136.63
130.24
130.11
116.20
115.85
77.67
77.16
76.65
66.54
49.29
34.86
f1 (ppm)

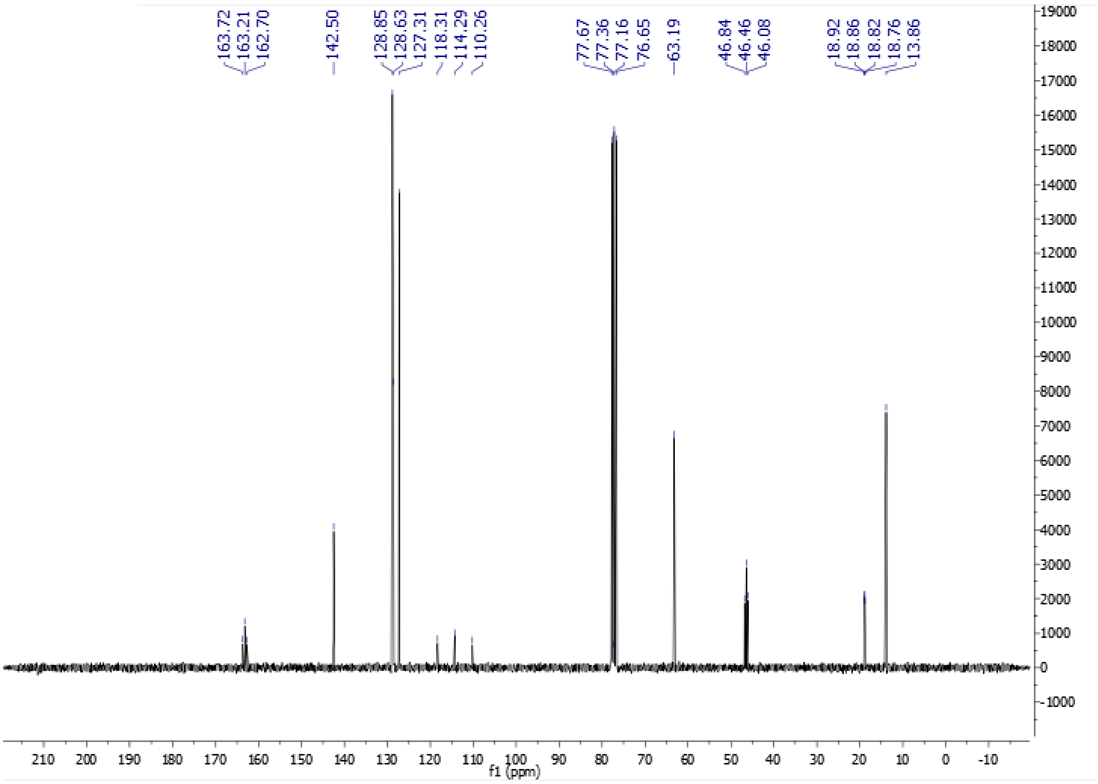
Compound **9f**


7.42
7.40
7.37
7.28
7.26
7.22
7.19
7.16
5.36
5.34
5.33
5.31
4.17
4.15
4.11
4.09
4.07
4.03
4.01
2.38
2.36
1.55
Br
Br
Br
Br
H3C
2.00
2.13
1.00
2.08
3.23
f1 (ppm)

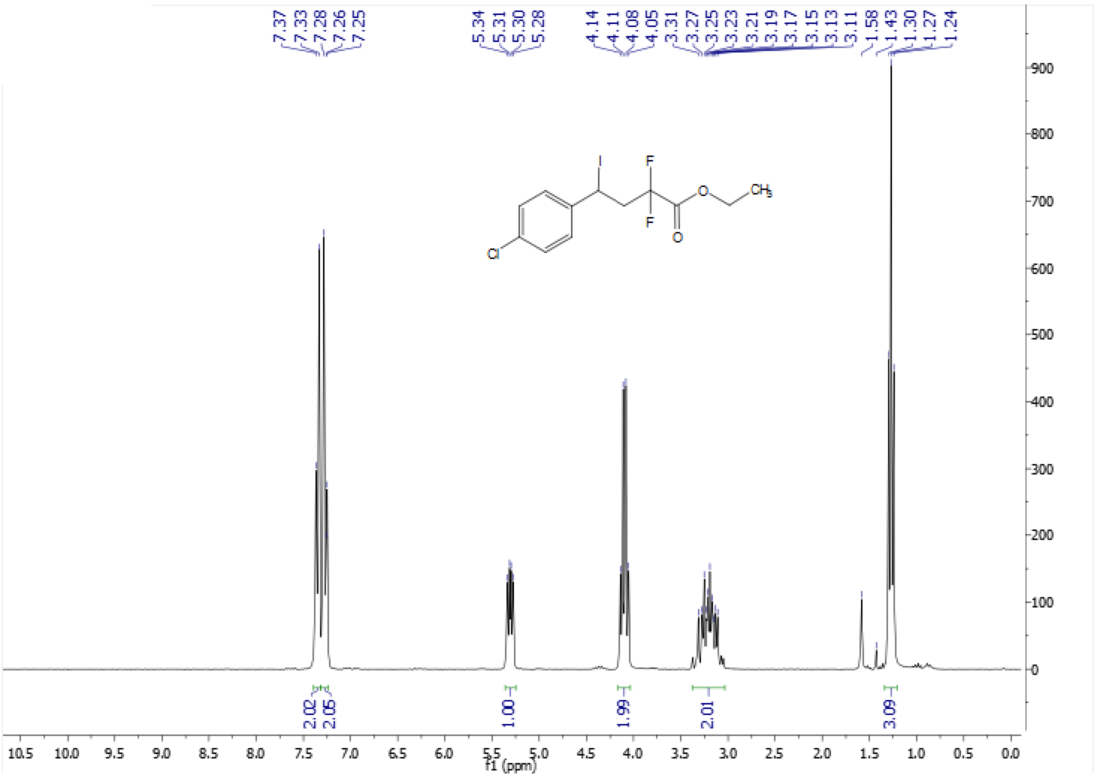

139.10
137.96
129.68
128.16
77.67
77.16
76.65
66.55
50.42
35.34
21.43
f1 (ppm)

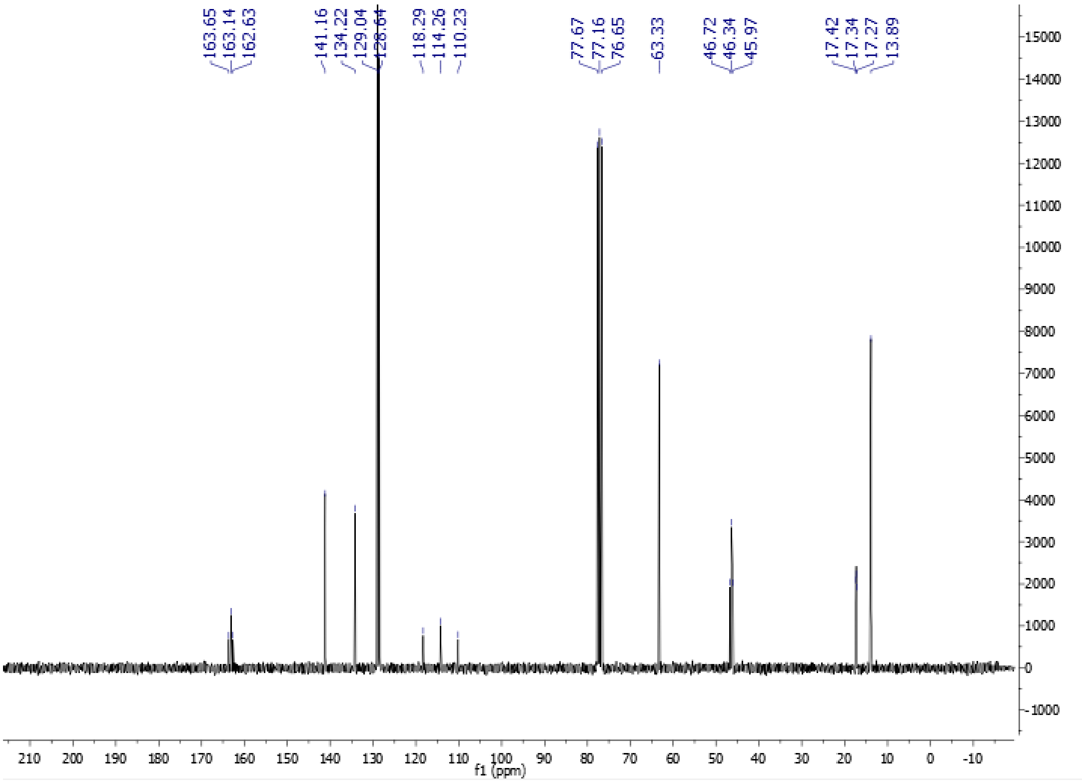
Compound **11a**



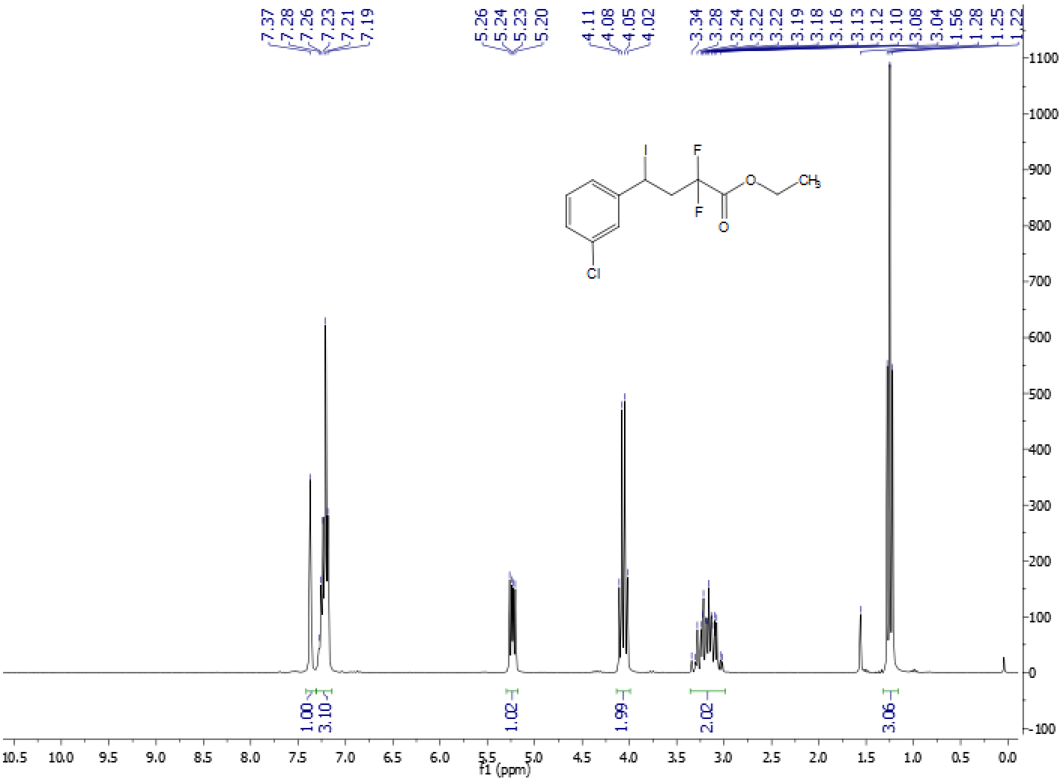


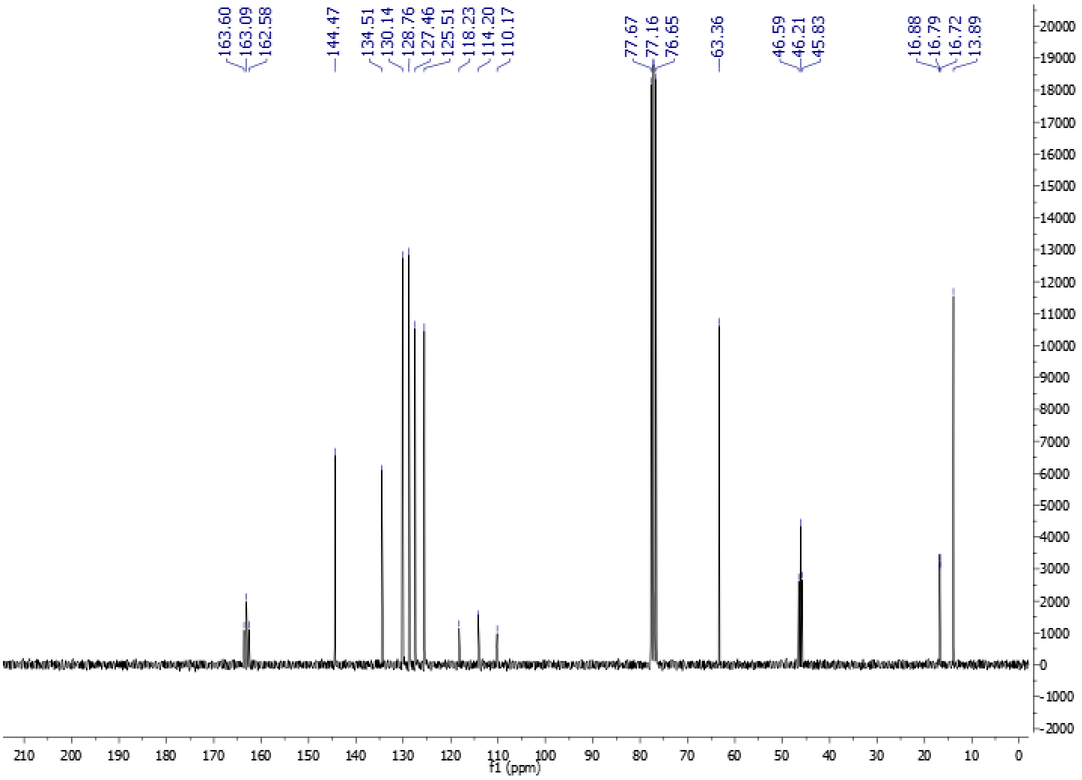
Compound **11b**



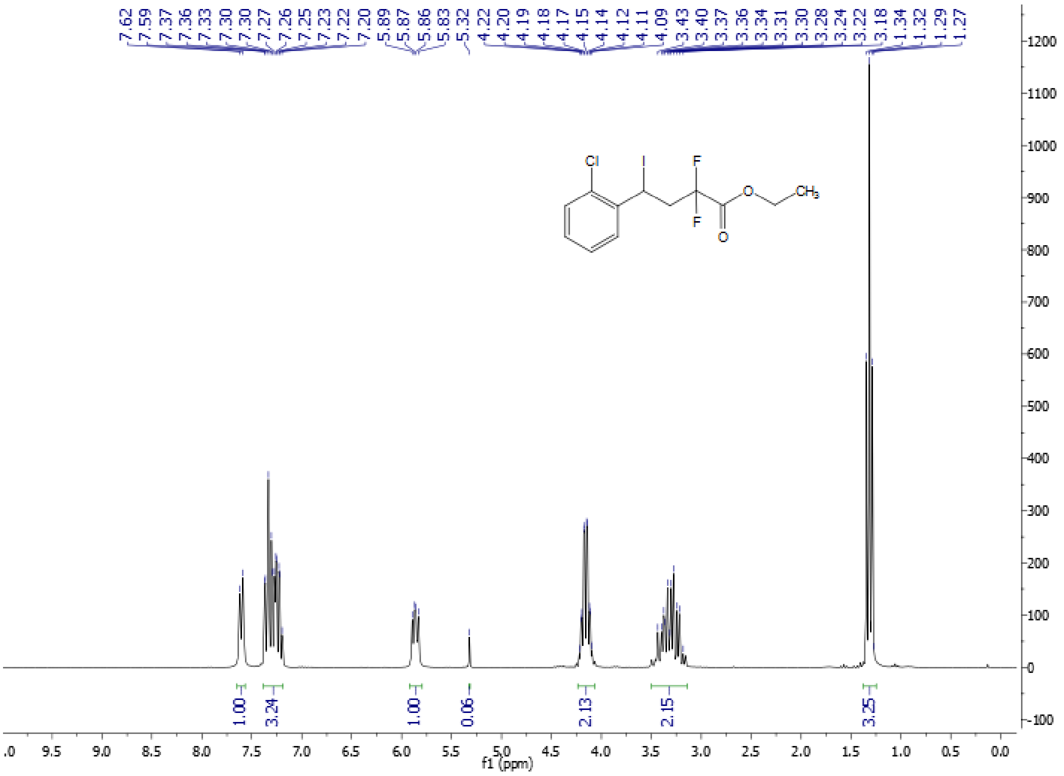


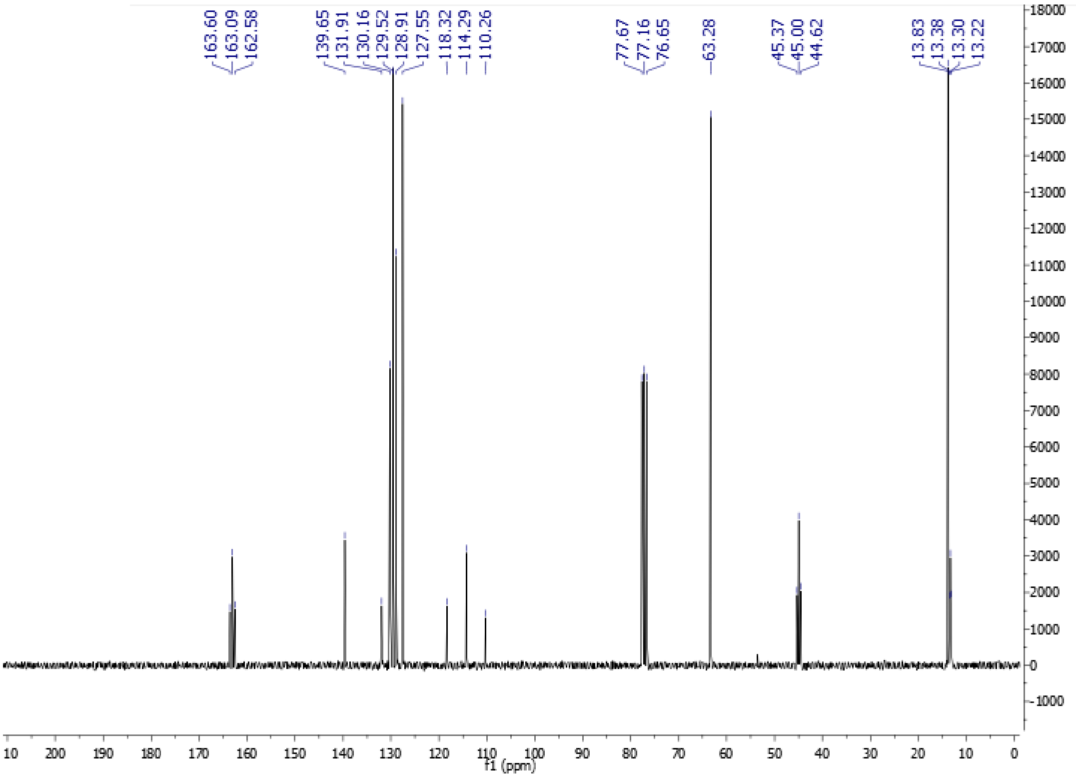
Compound **11c**



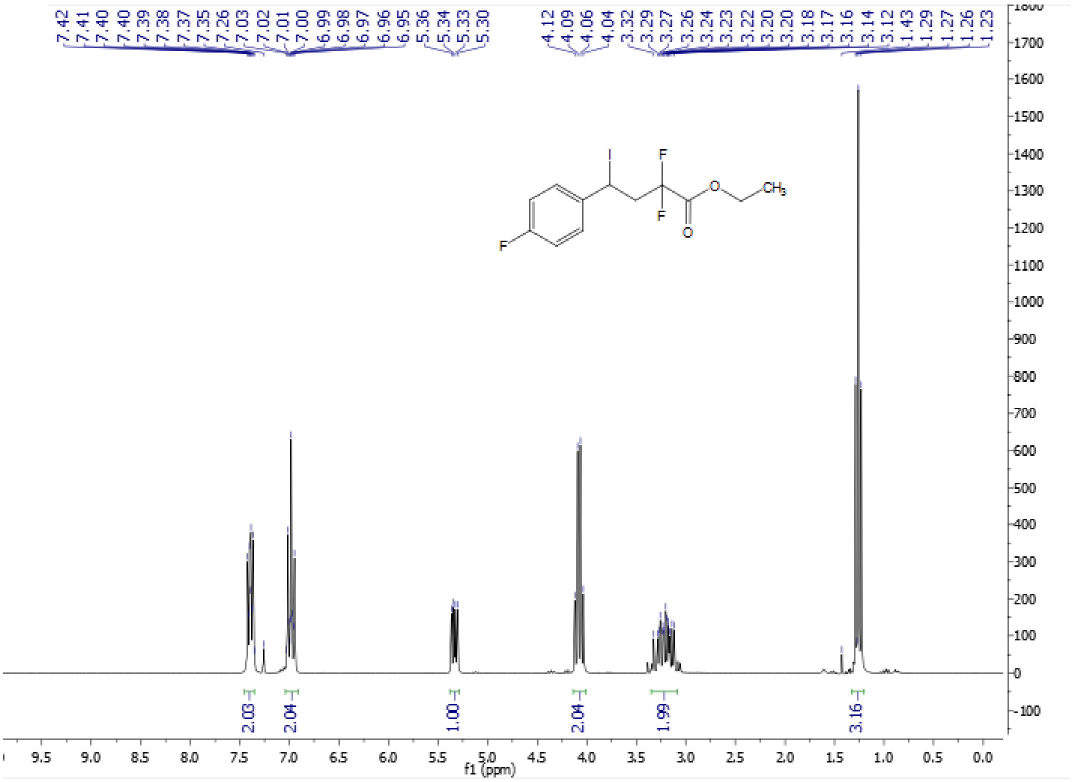


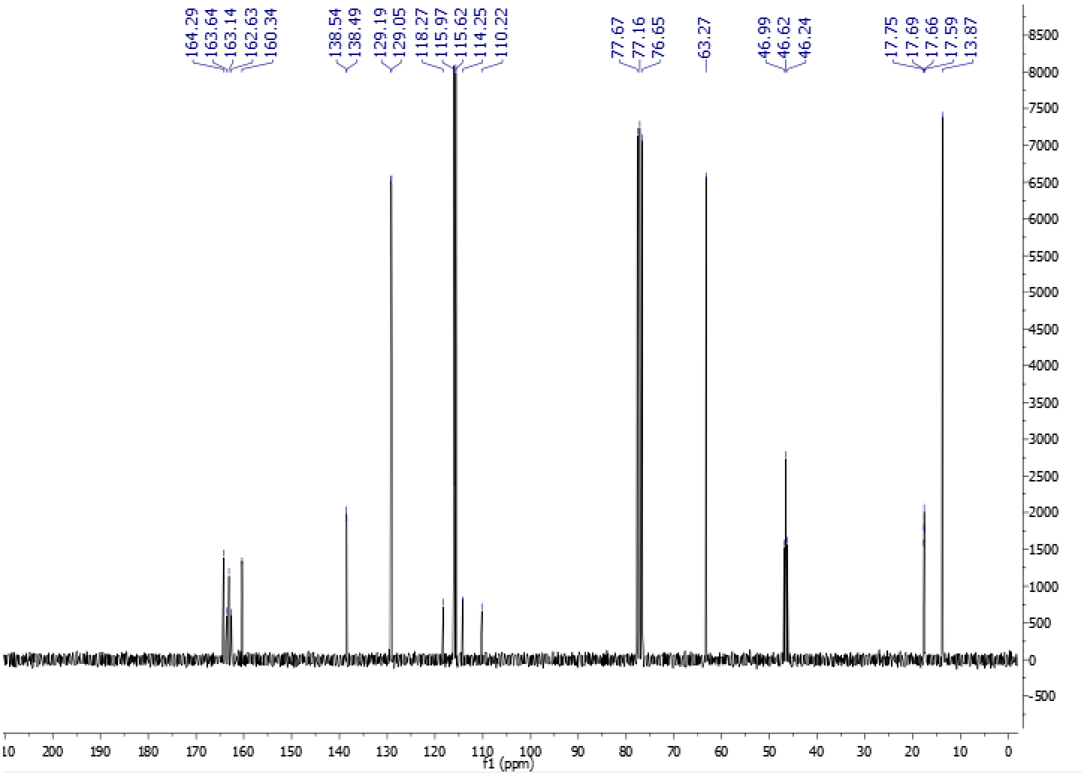
Compound **11d**



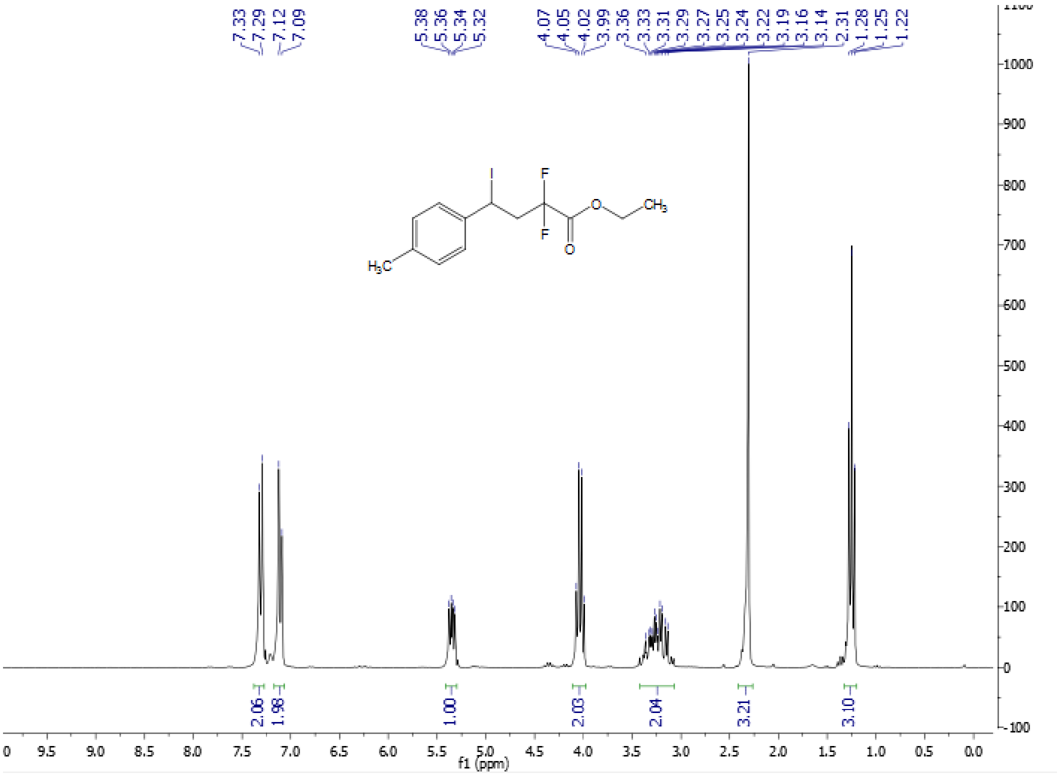


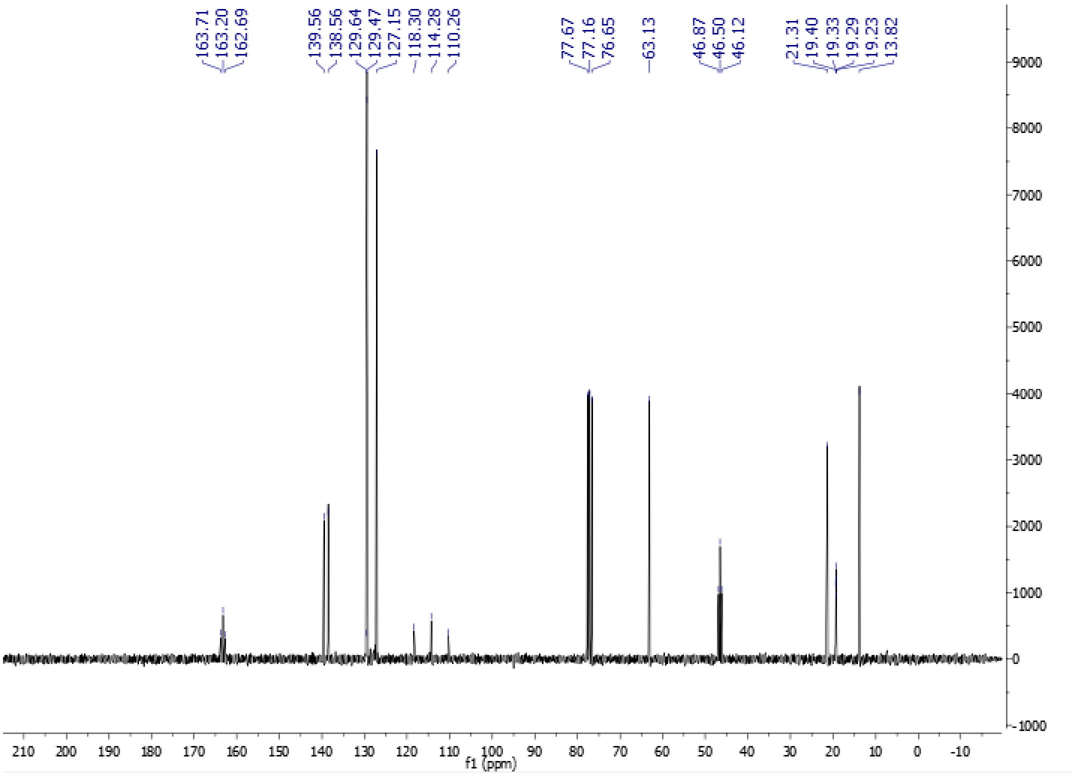
Compound **11e**



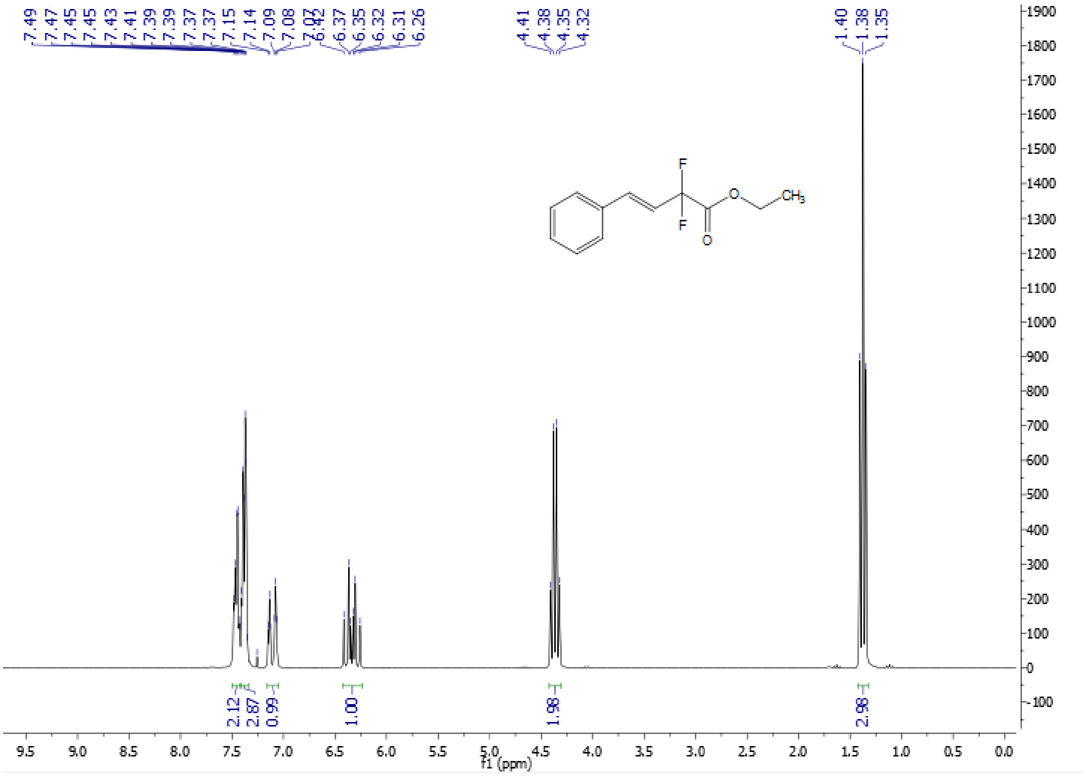


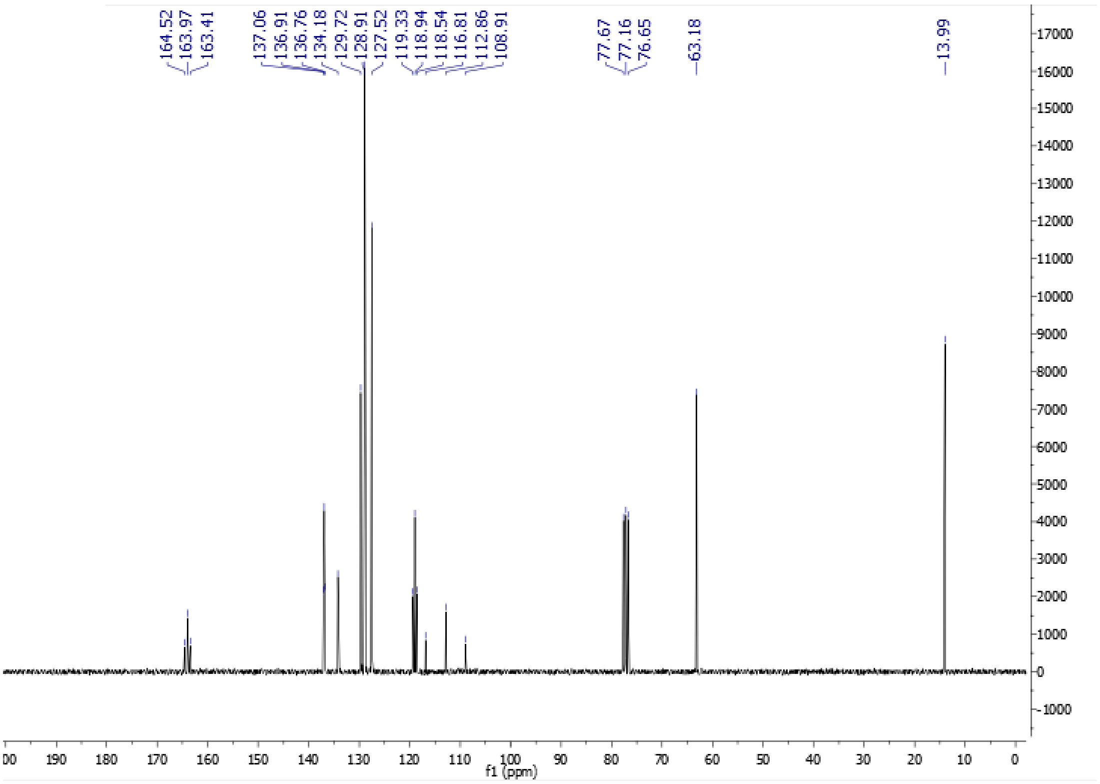
Compound **11f**



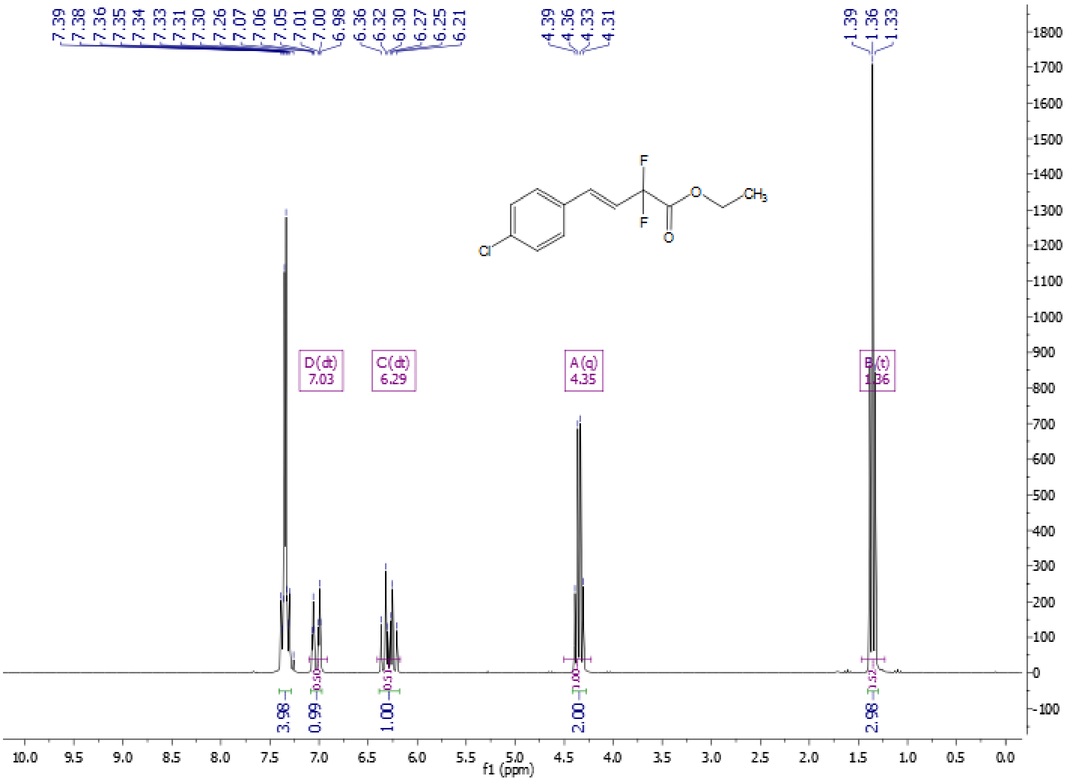


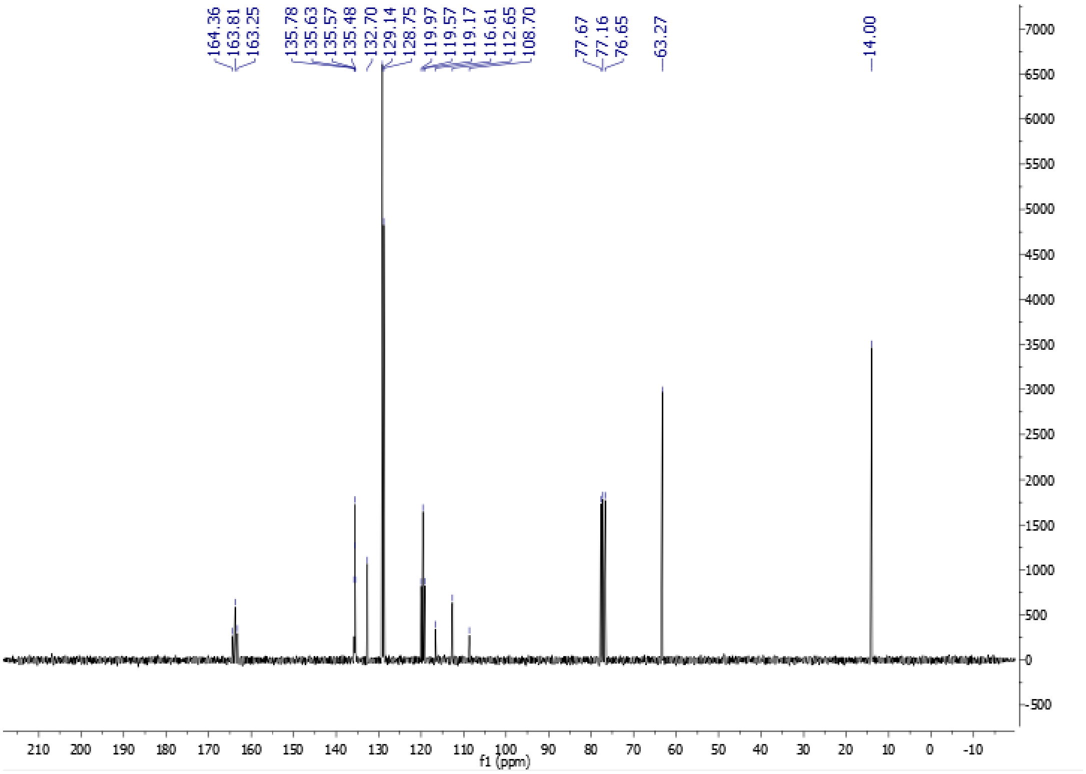
Compound **12a**





Compound **12b**





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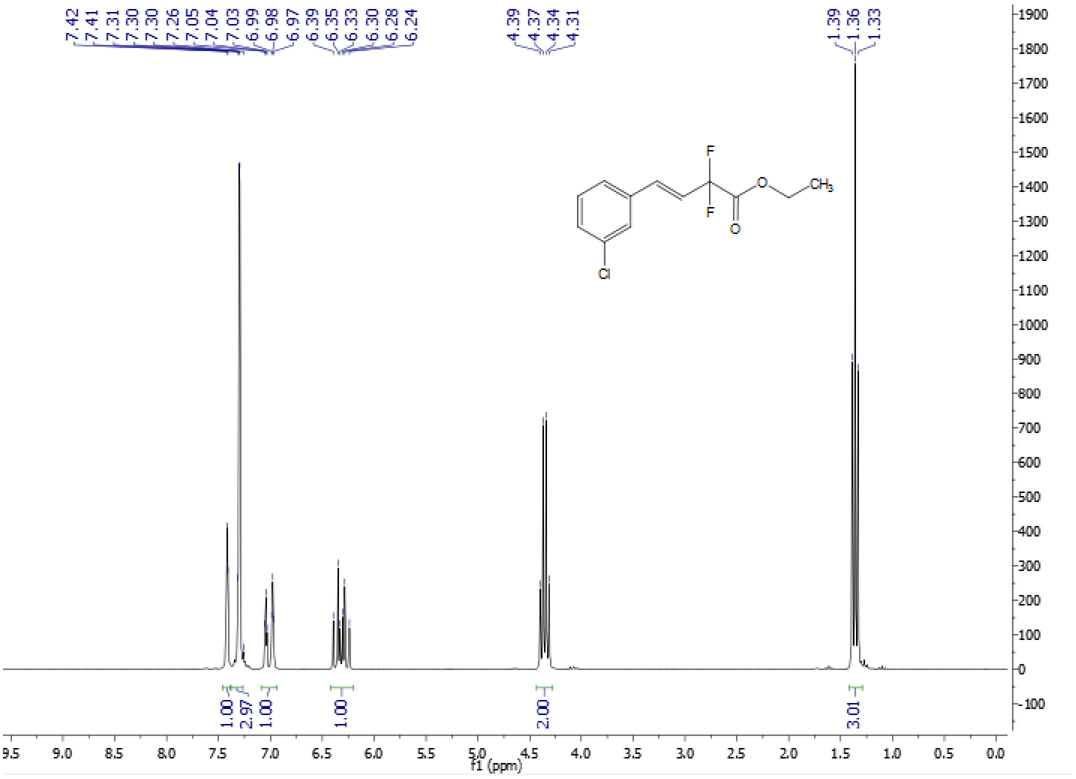

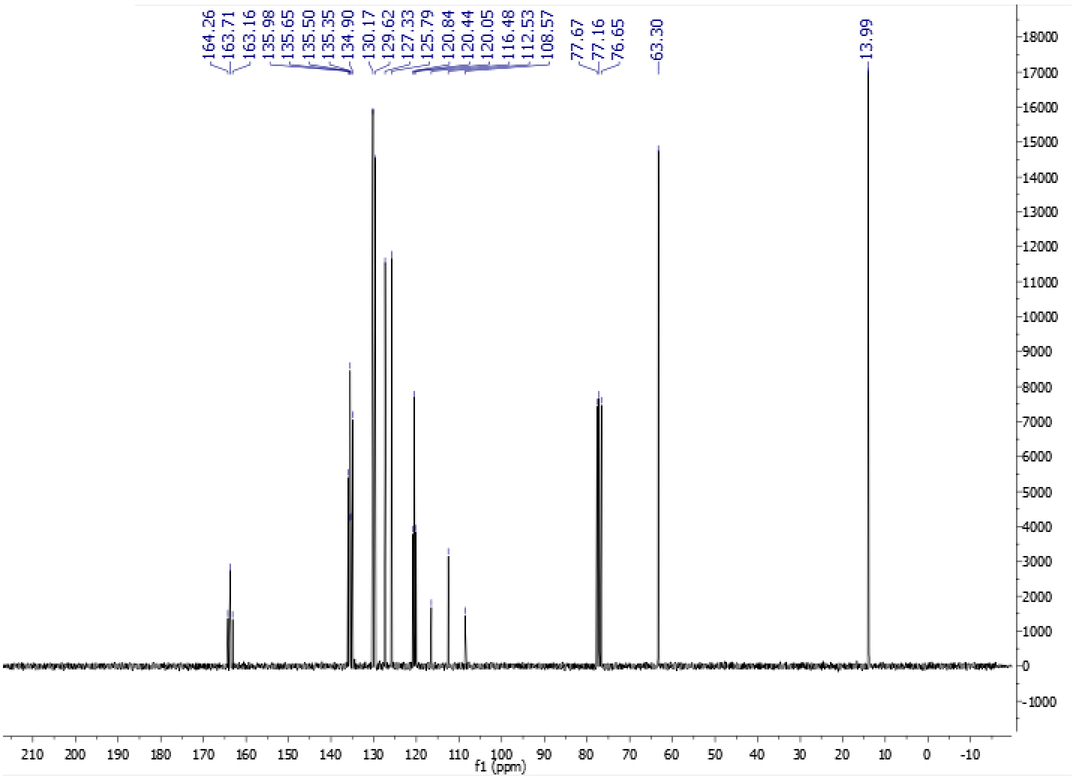

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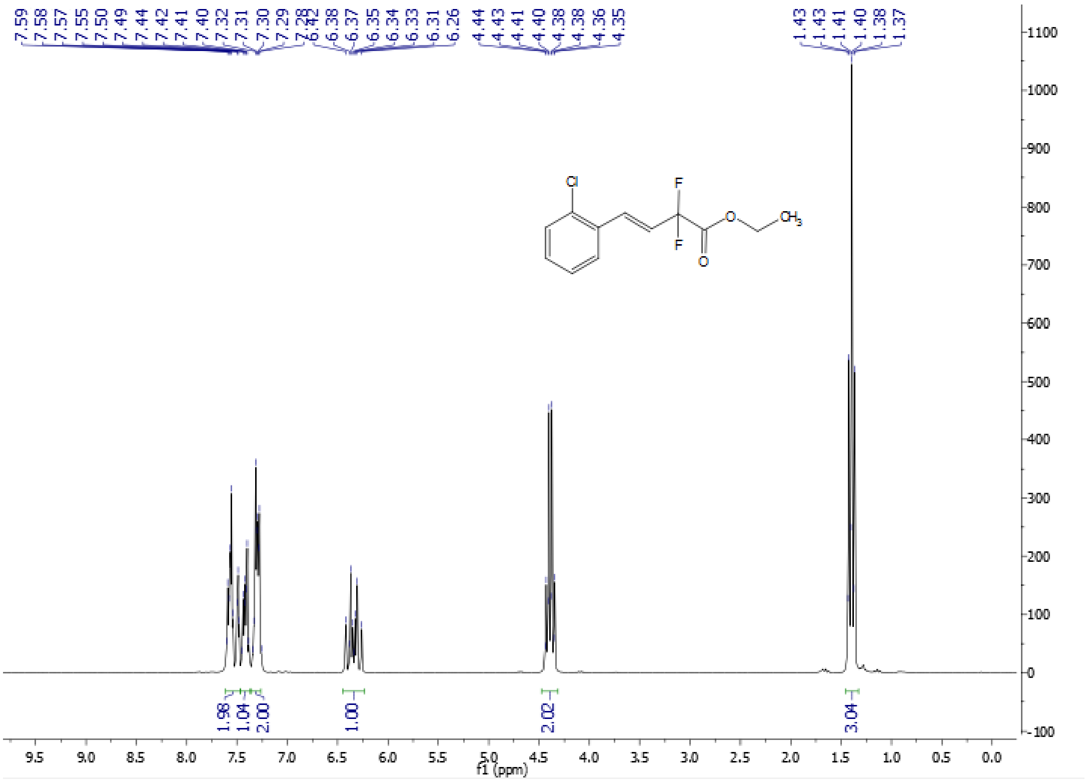

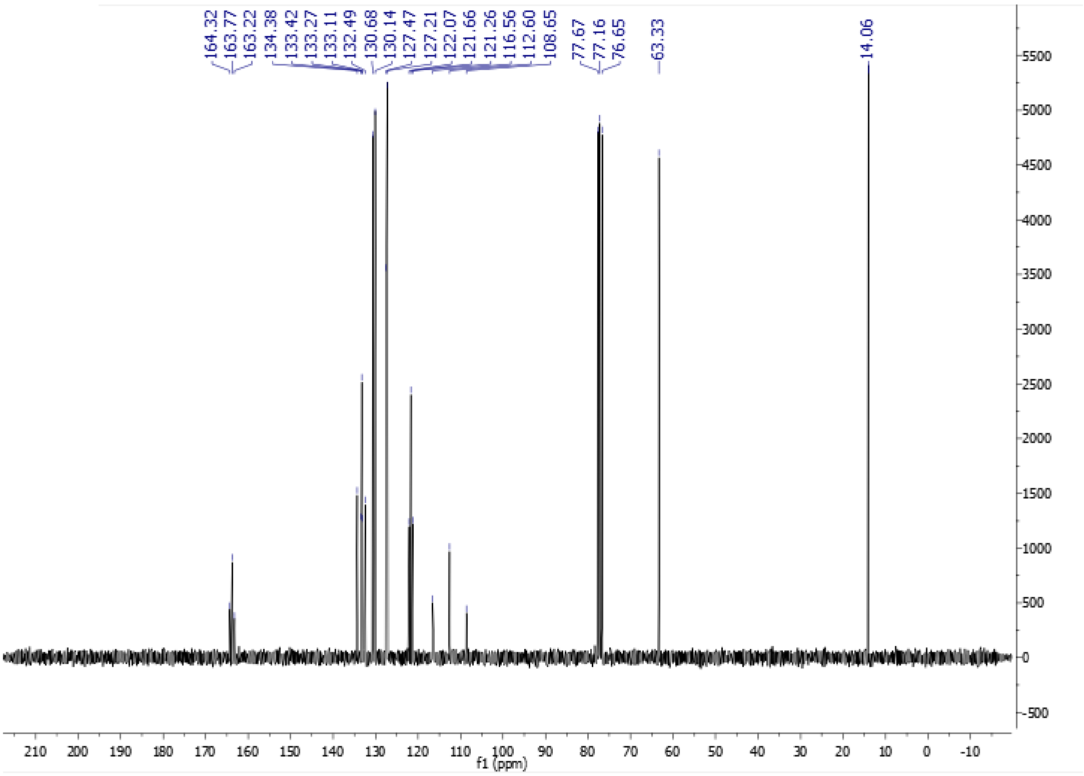

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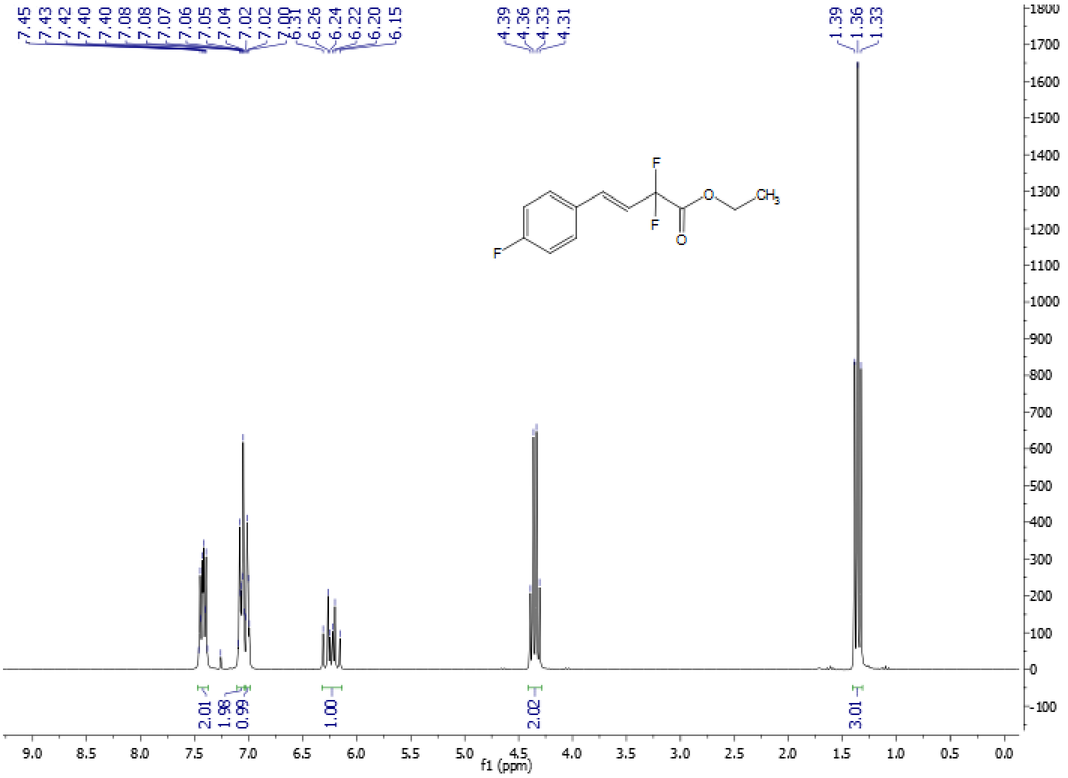

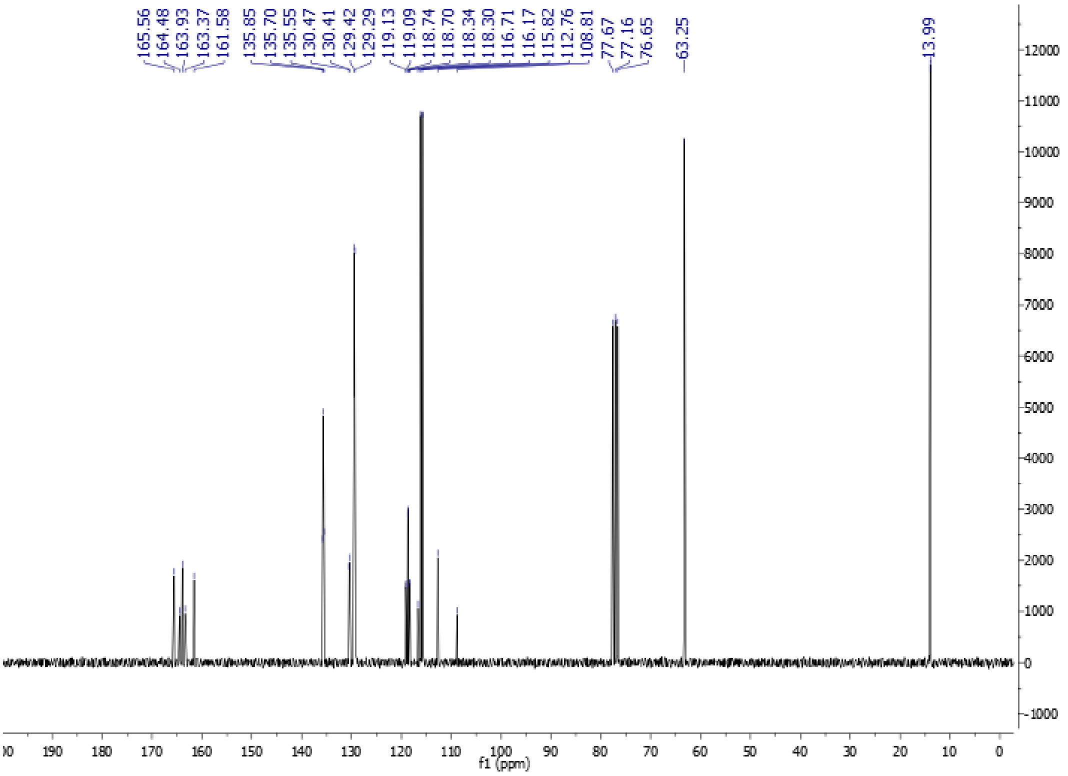

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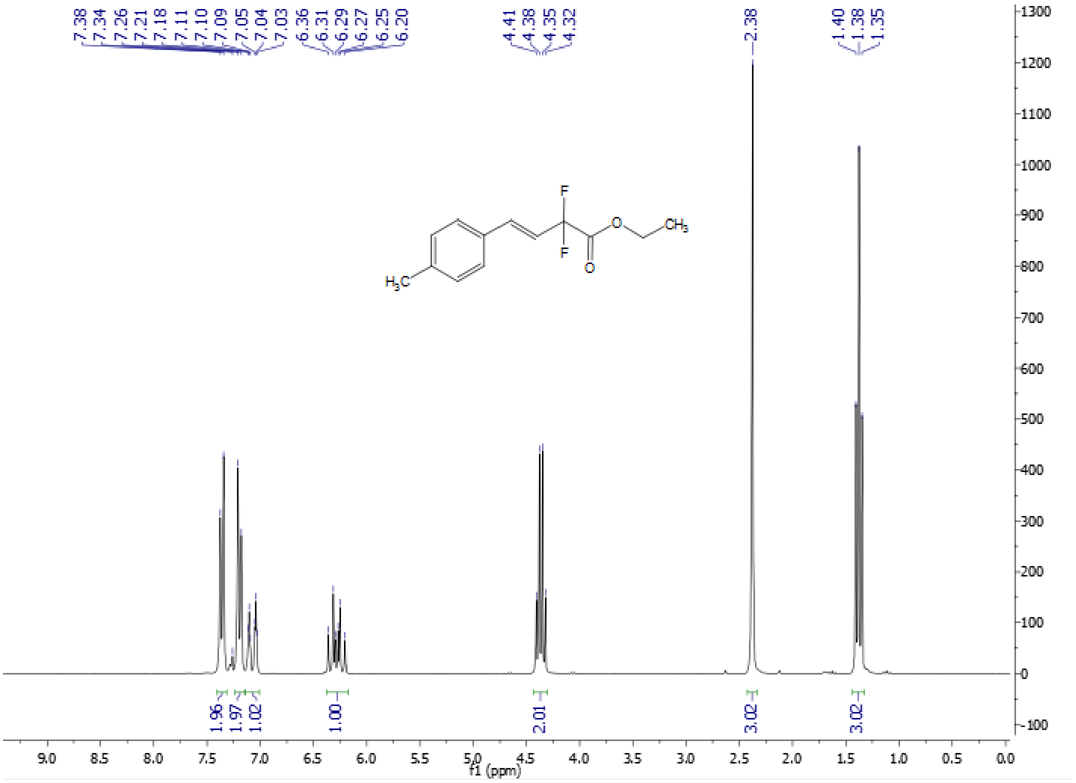
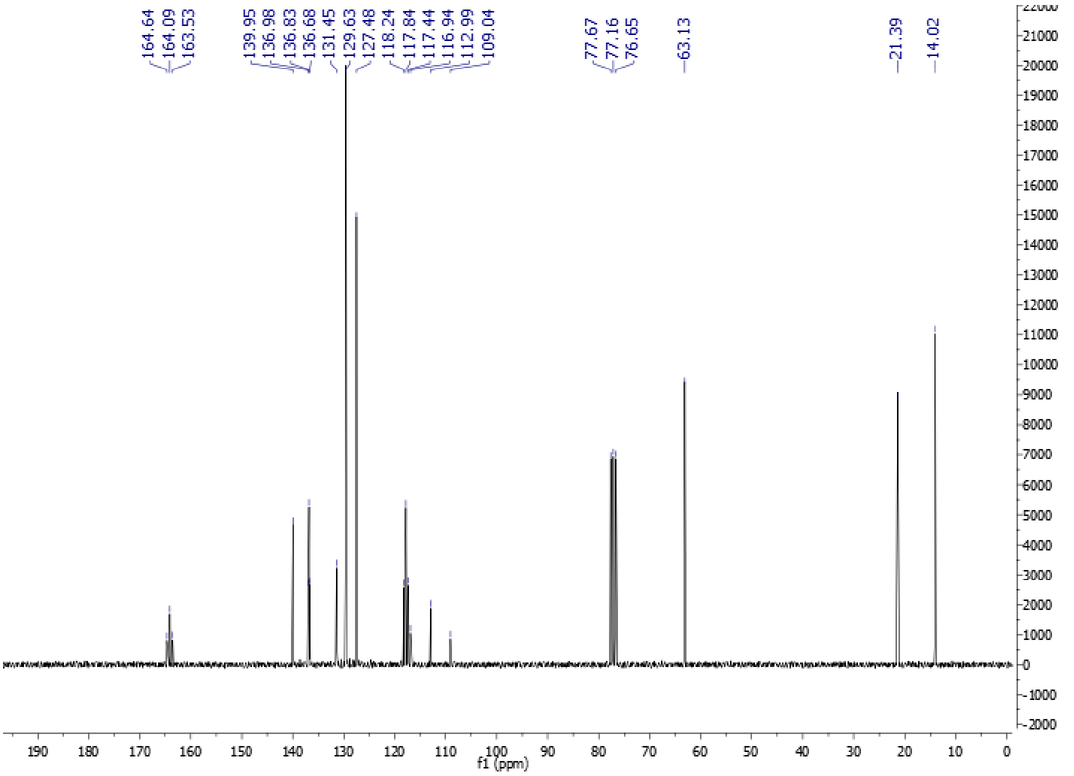
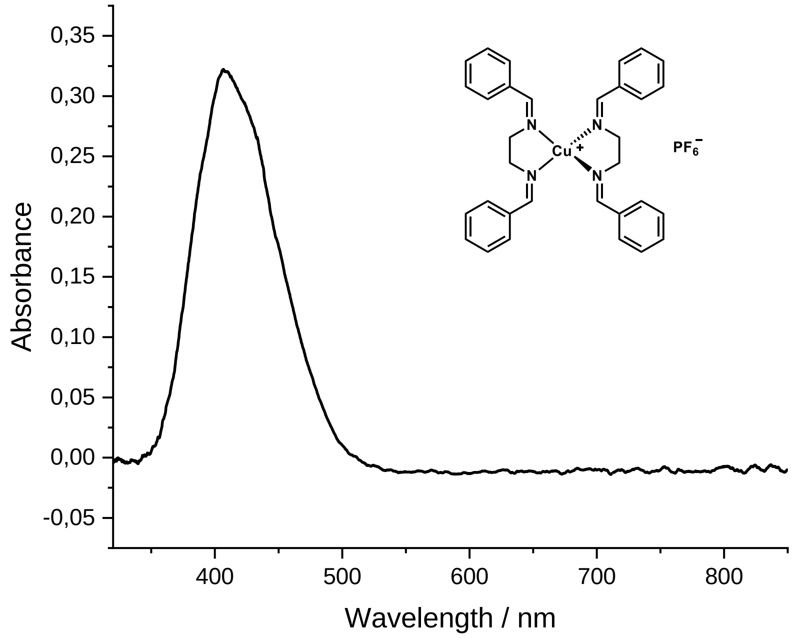




UV-VIS spectra of the copper complexes

Compound **6a**



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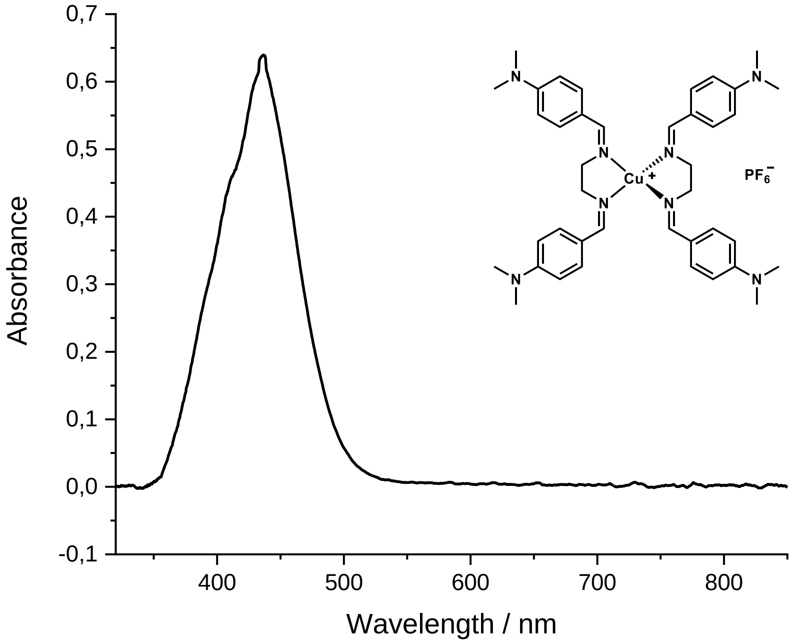

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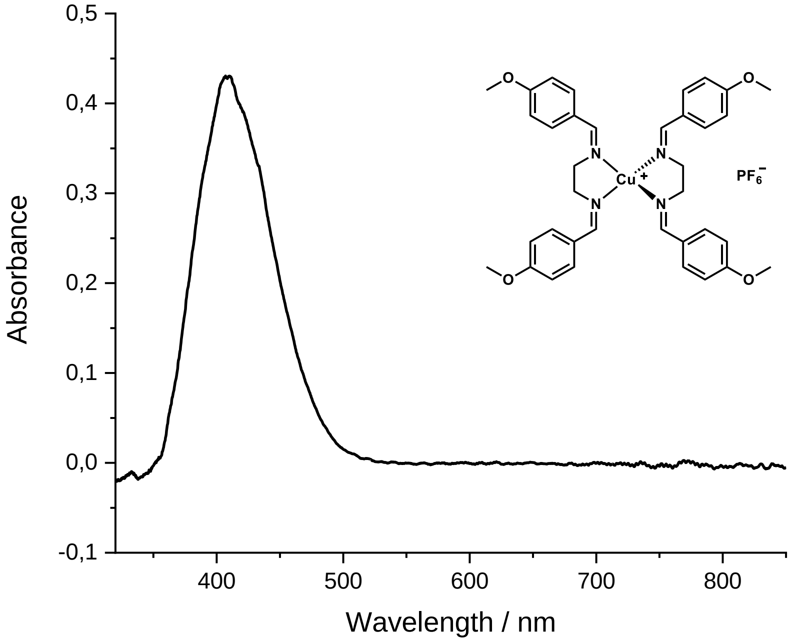
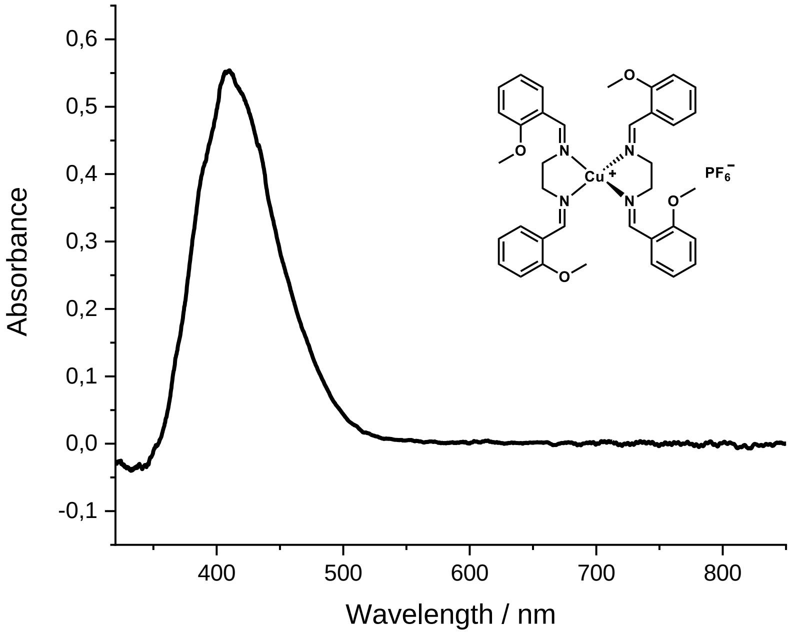


Compound **6d**



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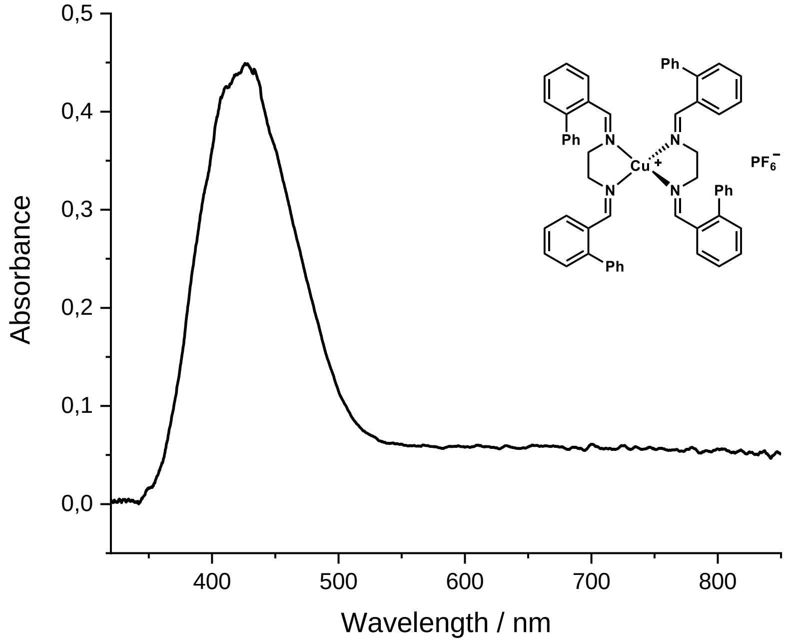

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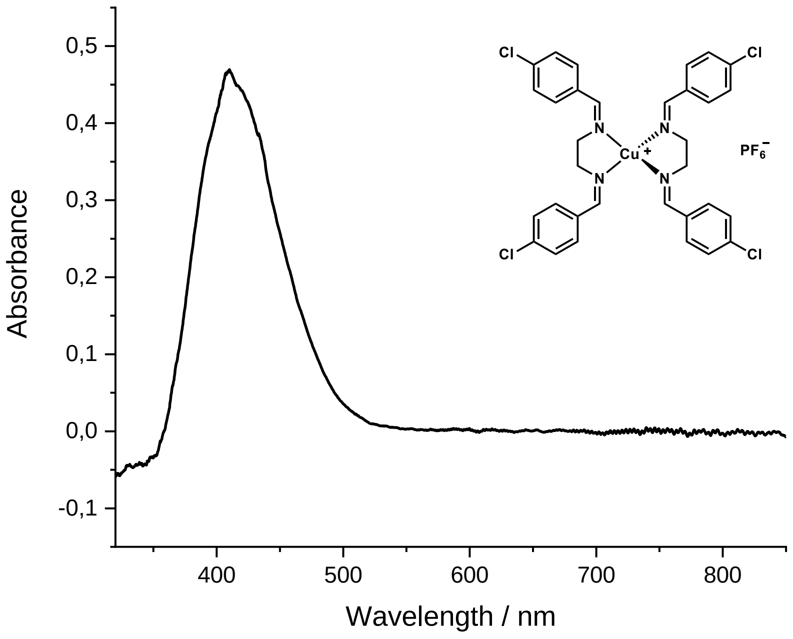
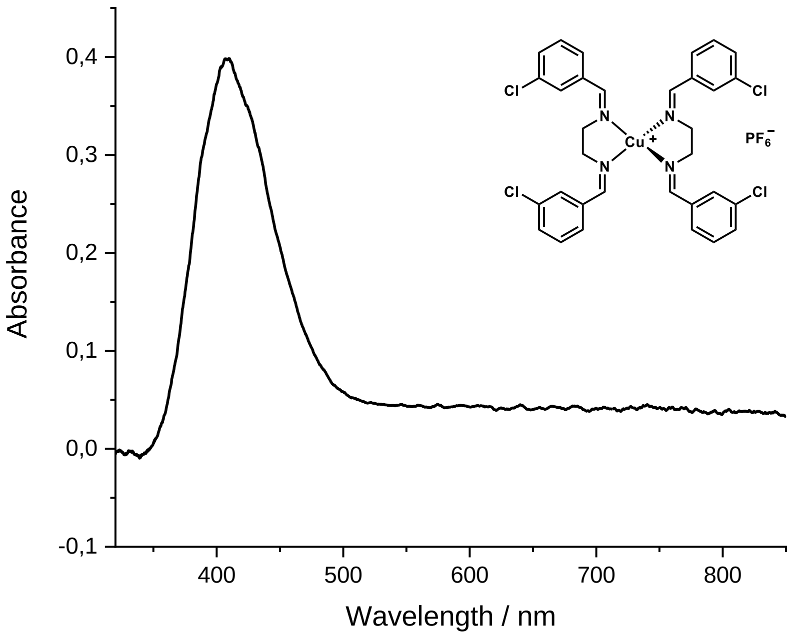
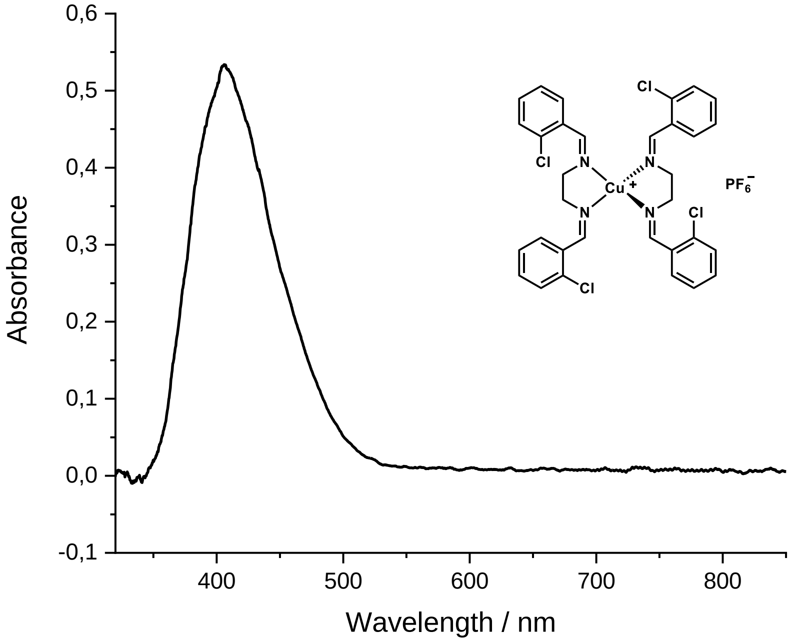


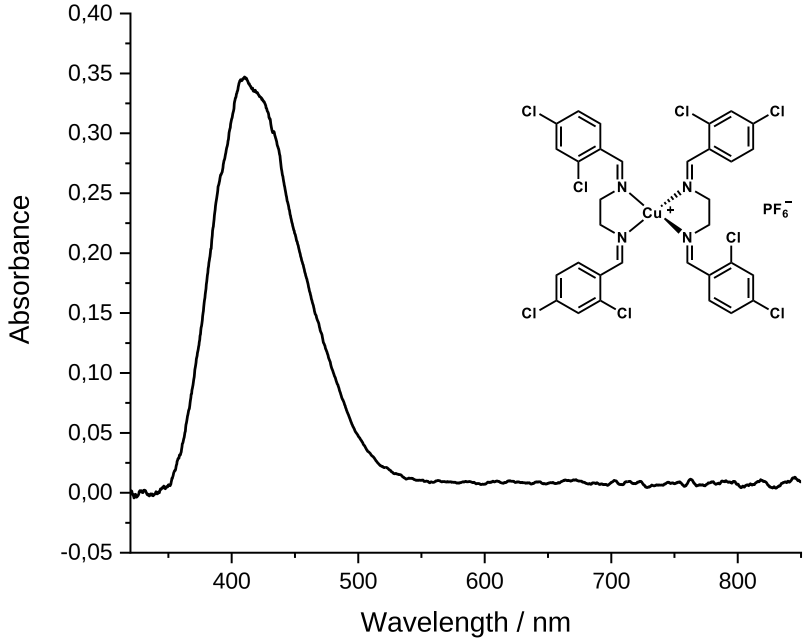
Compound **6g**



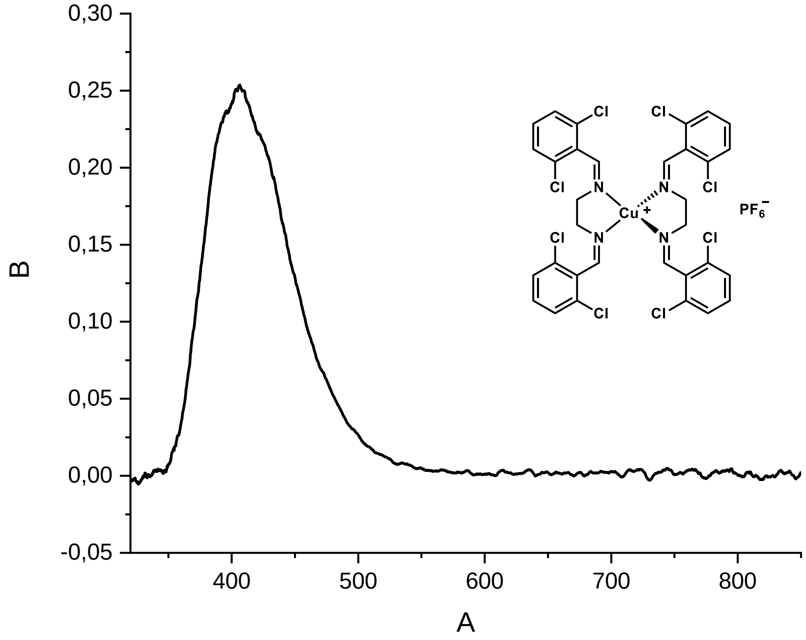
Compound **6h**



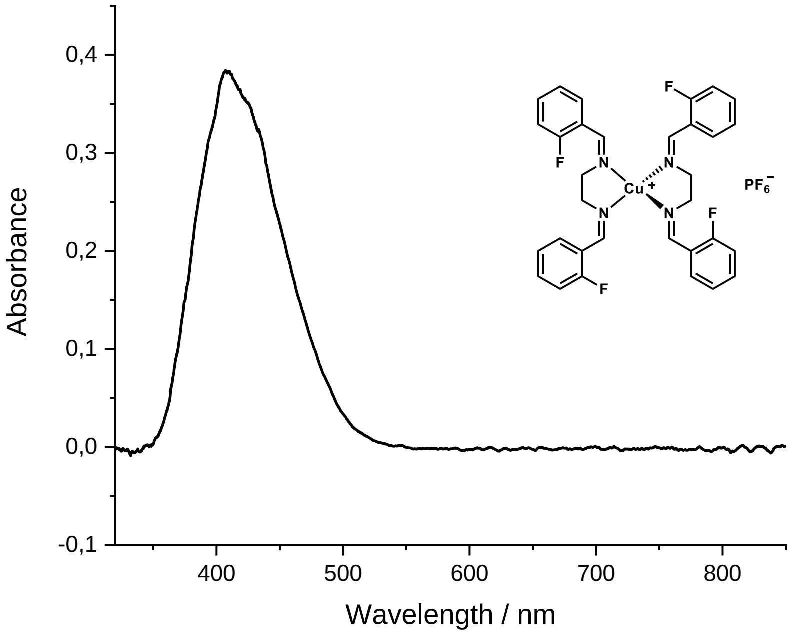
Compound **6i**



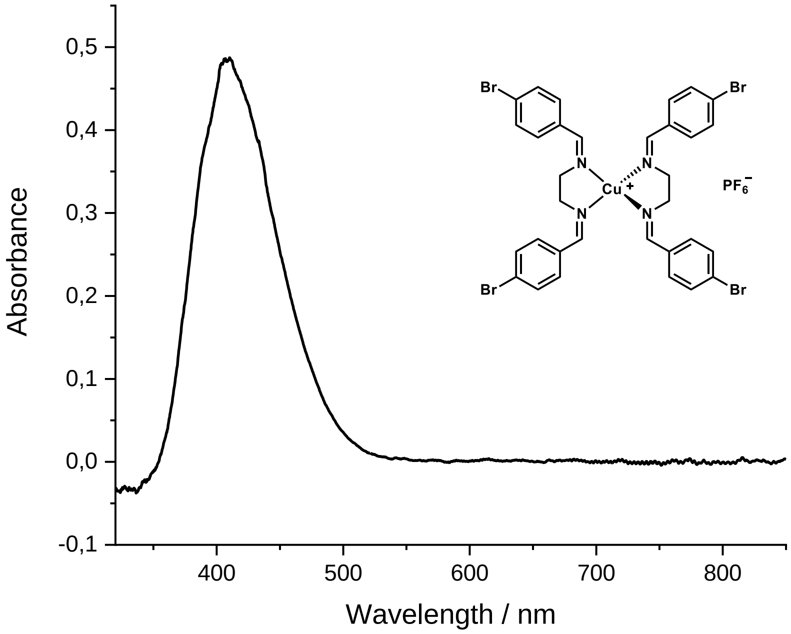
Compound **6j**



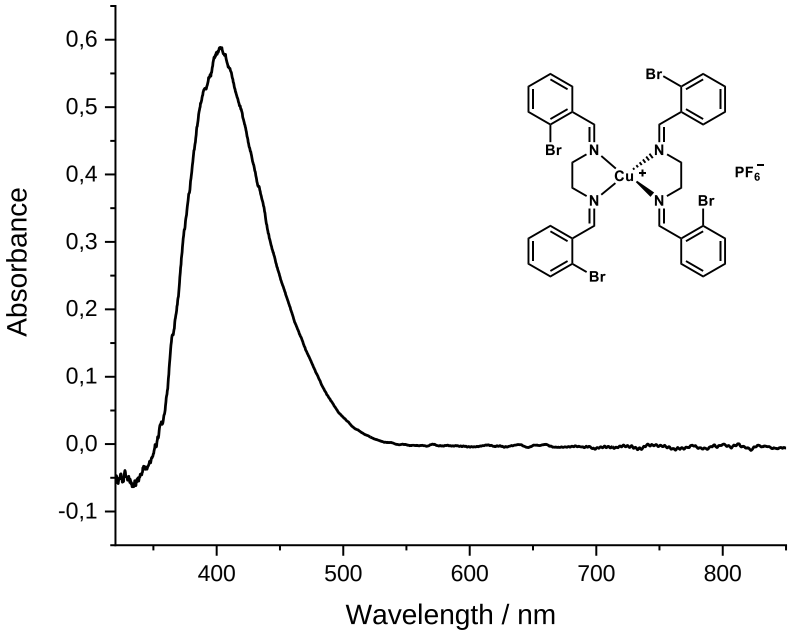
Compound **6k**



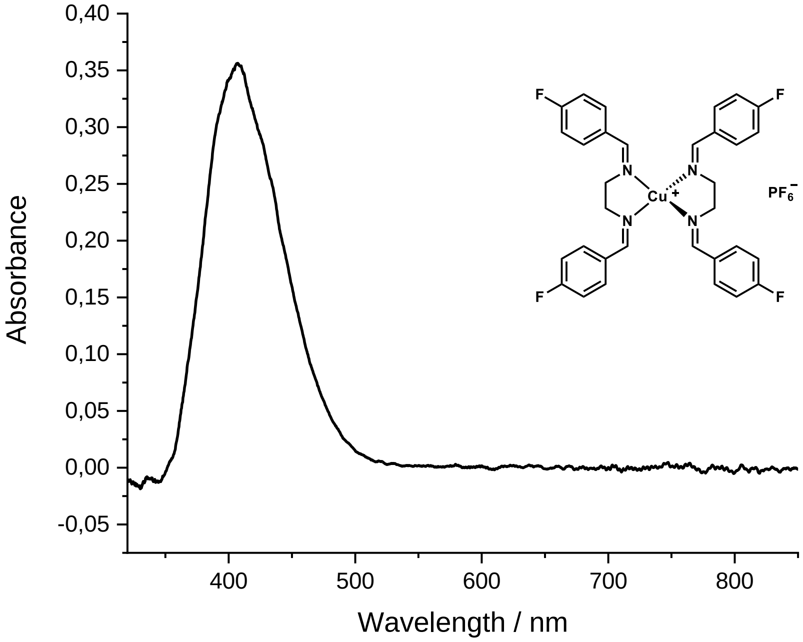
Compound **6l**



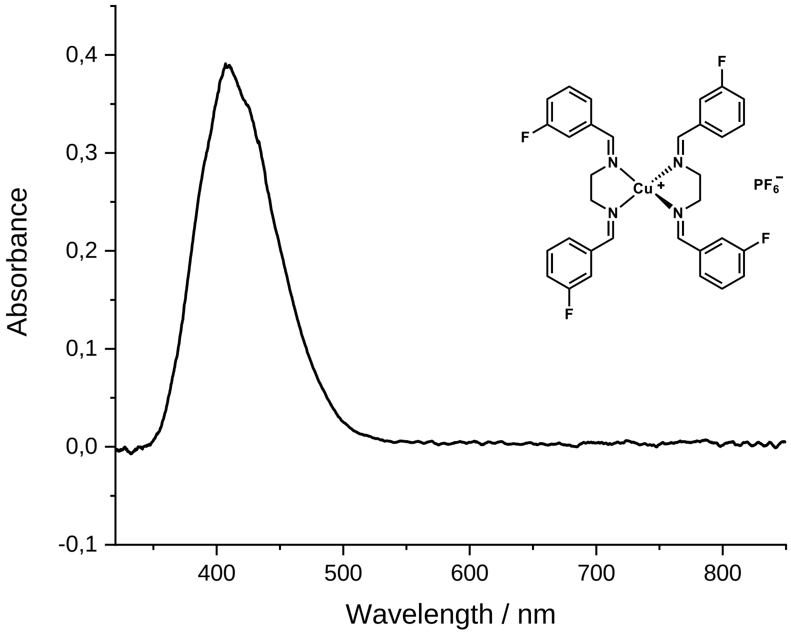
Compound **6m**



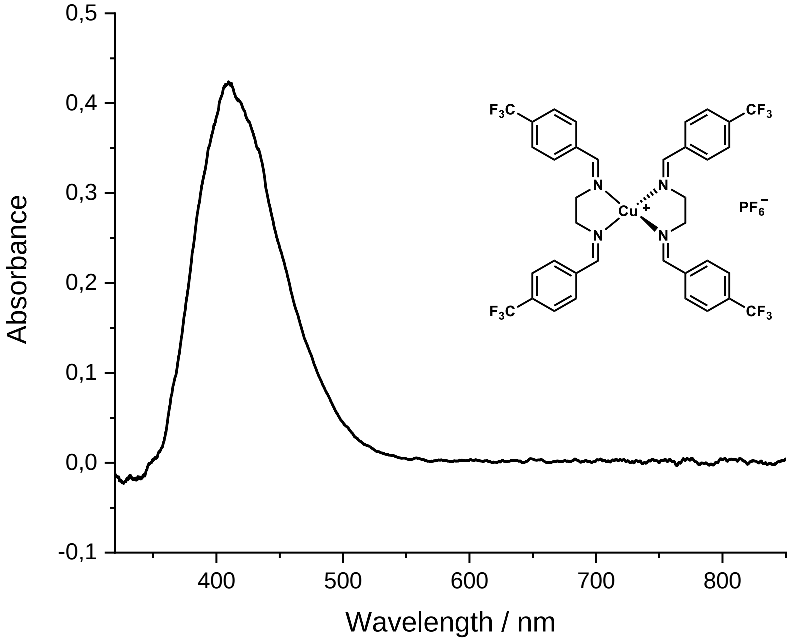
Compound **6n**



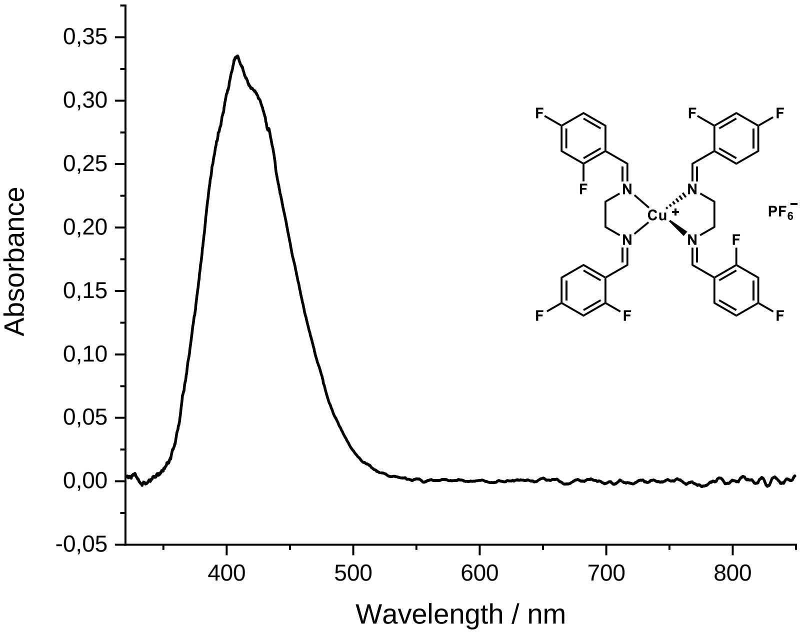
Compound **6o**



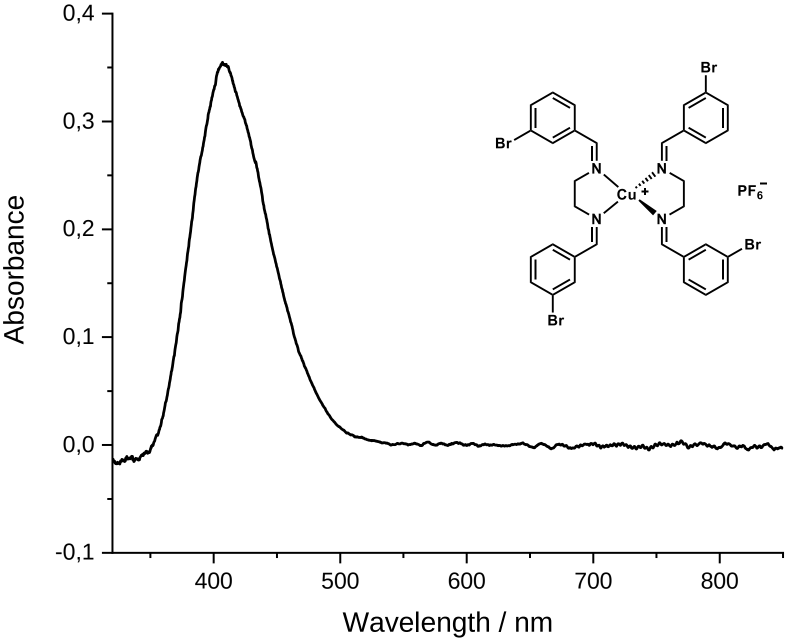
Compound **6p**



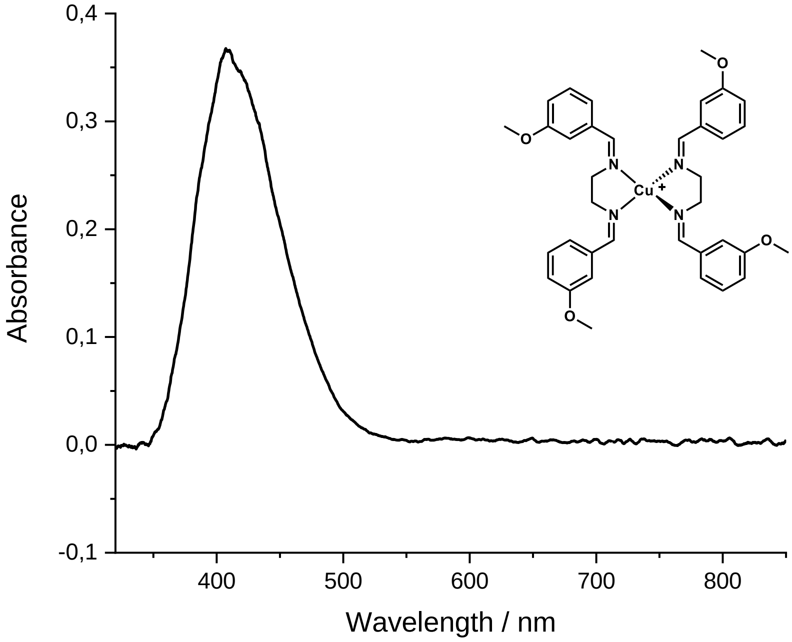
Compound **6q**



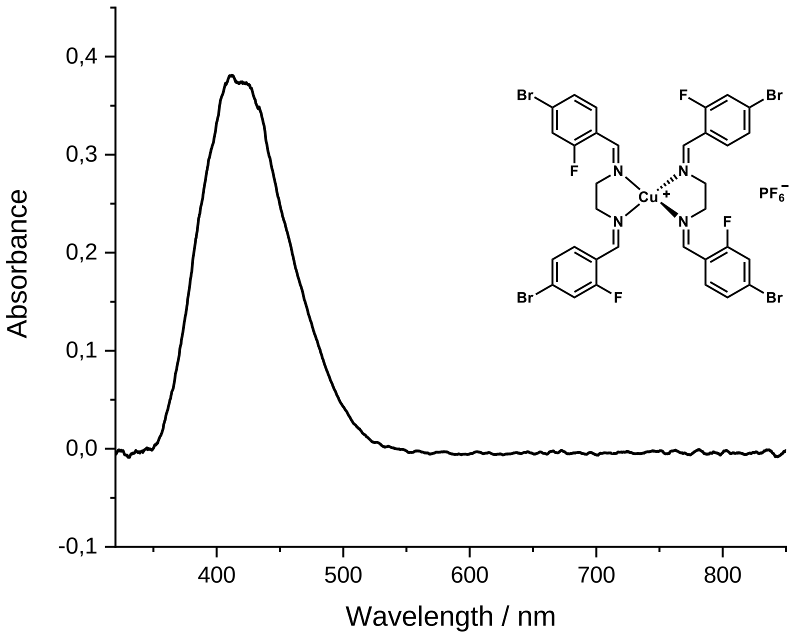
Compound **6r**

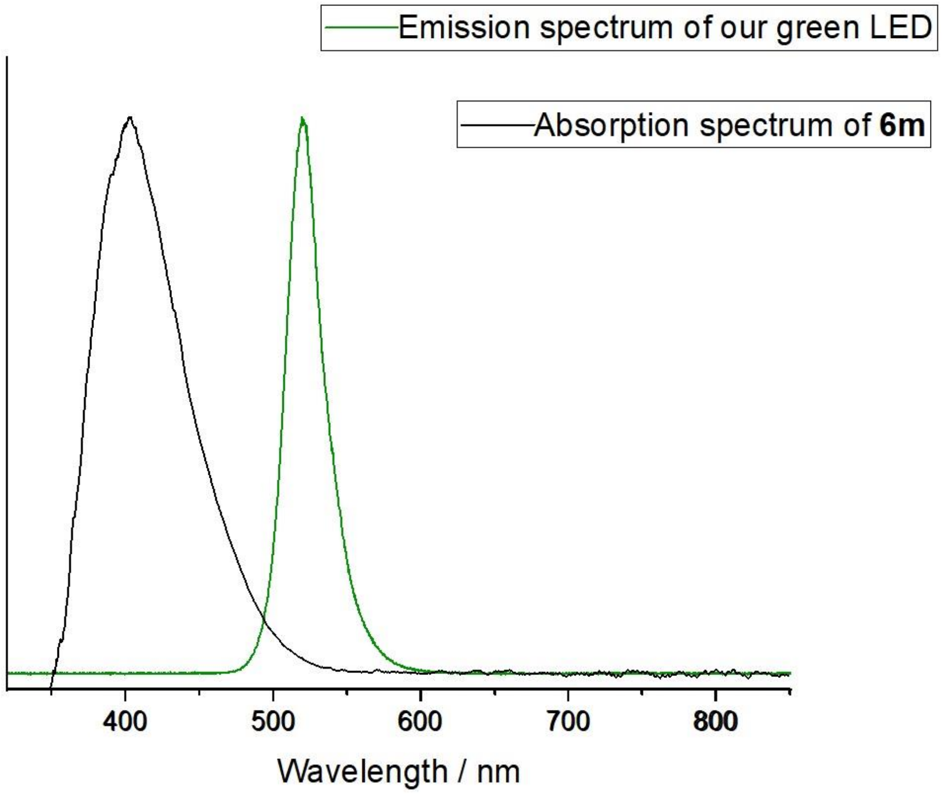


Compound **6s**



Compound **6t**




Emission spectrum of our green LED
Absorption spectrum of **6m**
400
500
600
700
800
Wavelength / nm

Photophysical measurements

The absorption spectra were recorded on a Unicam UV500 spectrophotometer with a resolution typically of 1 nm. The fluorescence spectra were measured on a Jasco FP 8300 equipment using typically 5 nm resolution, when the excitation wavelength was typically 378 or 420 nm. The fluorescence decays were recorded by an Edinburgh Instruments FLS 920 time-resolved spectrofluorometer, using an EPL-375 semiconductor laser (378 nm) for excitation and a Hamamatsu R3809U-50 MCP-PMT for detection. In transient absorption (TA) measurements the excitation wavelength was 355 nm from a frequency-tripled Nd:YAG laser (Continuum Surelight), with a typical energy of 50 mJ/flash. 2-4000 signals were averaged in a Tektronix TD4 640A recorder to improve the signal to noise ratio.

The tails of the absorption spectra reach the green light region, although the main absorption bands with considerable molar absorption coefficient belongs to the near UV and blue regions. The fluorescence intensity is very week for both **6m** and **6d** in the applied solvents (around 10^{-2}, see **Table SI**). The main component of the corresponding fluorescence decays is in the 30-40 ps range, which surely too short for a bimolecular reaction. The longer components has much smaller preexponential factors, and considering the small fluorescence yields, they may related to contaminants too.

Table SI. Some fluorescence yield and decay parameters of two catalysts in acetonitrile and dichloromethane.
The fluorescence decays were multi-exponentials and given as $I_f(t) = \Sigma\ (A_i \exp(-t/\tau_i))$.

compound	solvent	Φ_fx10^5	τ_1 / ps	A_1	τ_2 / ns	A_2	τ_3 / ns	A_3	τ_4 / ns	A_4
6m	MeCN	**0.5**	**35**	**1**	1.05	0.08	4.9	0.02	18.5	0.005
6m	DCM	**1**	**29**	**1**	1.47	0.05	5.2	0.02		
6d	MeCN	**2**	**44**	**1**	0.42	0.20	3.1	0.03	13	0.008
6d	DCM	**0.5**	**86**	**1**	1.24	0.20	5.9	0.13		

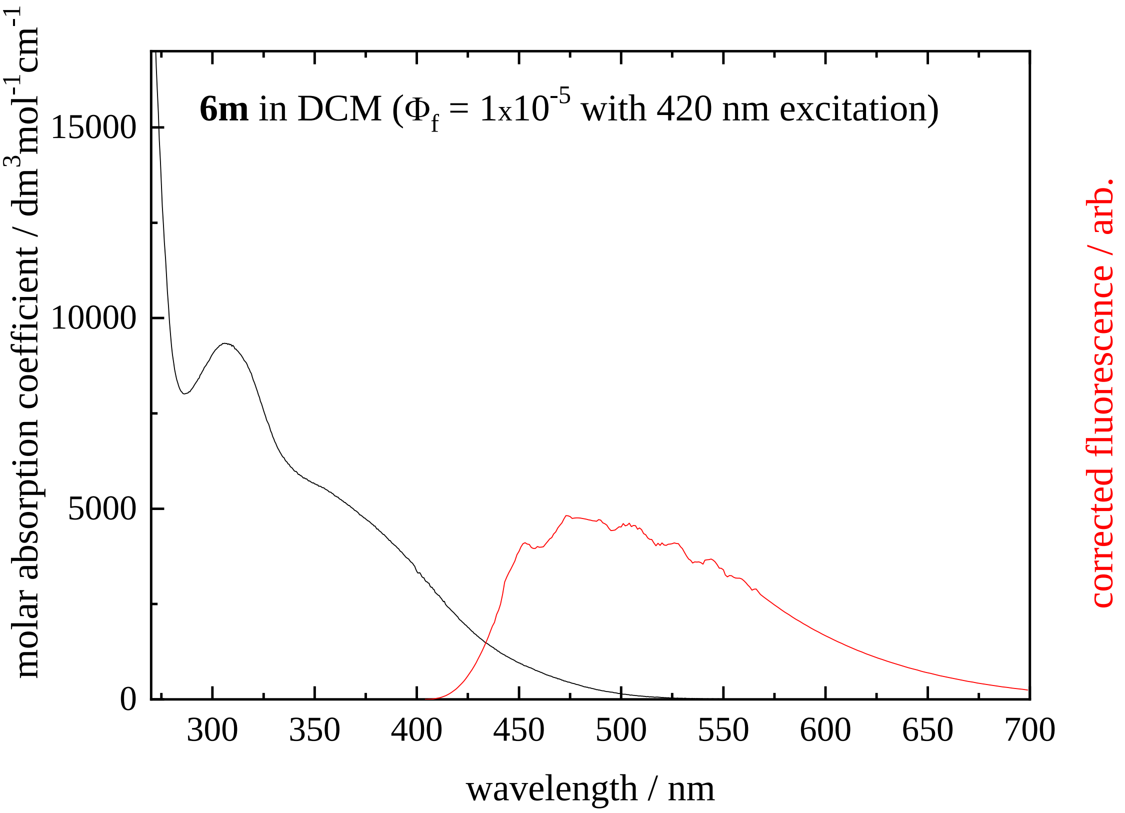


Figure SI1. Absorption and corrected fluorescence spectra (excited at 420 nm) of **6m** catalyzer in DCM. (The emission spectrum and fluorescence quantum yield moderately depends on the excitation wavelength.)

However, at 460 nm a long lived (30 ms) transient species was observed, while at 400 nm the (TA) signal appears in the opposite direction (i.e. $I > I_0$), which may be connected to the depletion of the ground state complex. The 30 ms lifetime is surely enough for a bimolecular reaction. The small signal is related partly to the fact, that both case the difference of the given molar absorption coefficients are in effect, and with slight red shift with excitation may results in the observed signals, especially when the triplet concentration is low. (In case of metal-organic complexes the higher energy excitation is not necessarily results only in the population of the lowest excited state, other channels may reach realization too.) An important observation to that contrary to styrene, in presence of CBr_4 a further increase of the 460 nm TA signal is detectable with a characteristic time constants 150 μs, which parameter is not depends on the CBr_4 concentration. This process may be interpreted that, there is a complex between this two molecules even in ground state, and after excitation, the complex changes the structure (see **Figure SI2**). This triplet induced mechanism has several appealing aspects which would require further studies, as we intend to do.

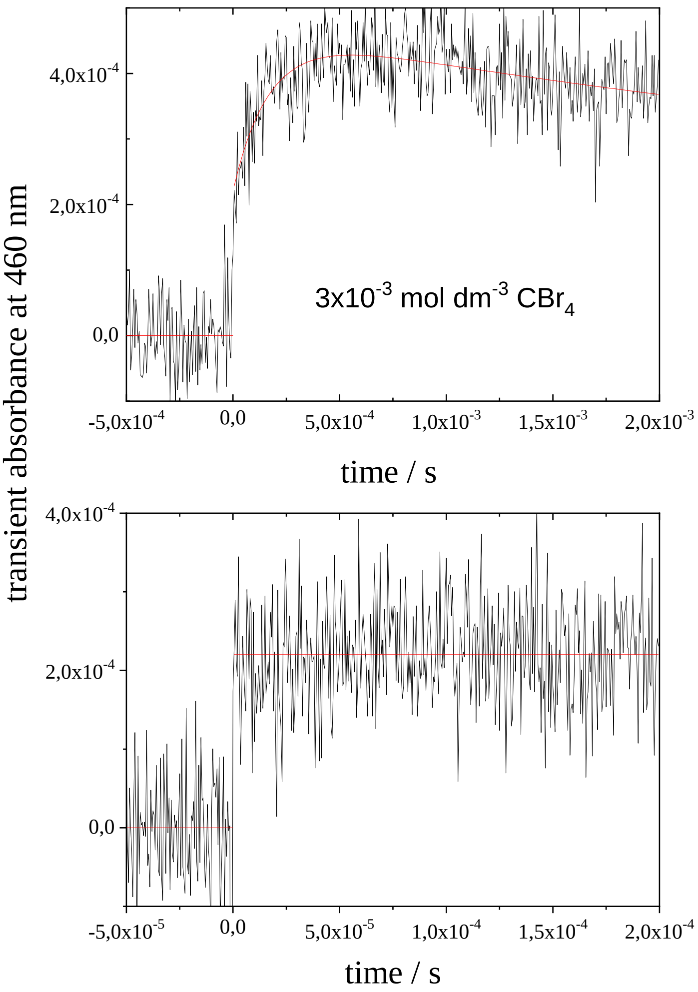


Figure SI2. Transient absorption signal at 460 nm; with $3x10^{-3}$ mol dm^{-3} CBr_4 additive (A). Similar measurement with $1x10^{-2}$ mol dm^{-3} styrene (B) where the timescale tenfold shorter. For excitation, the full light intensity of the third harmonic (355 nm) of a Surelight Nd-Yag laser was used, [**6m**] = $1.5x10^{-4}$ mol dm^{3} **6m** in DCM at 24 ^{o}C.

Electrochemical characterization of the bis(imine) based copper complexes

Experimental

All electrochemical measurements were carried out at room temperature (23.0 ± 0.5 °C). The solutions were purged with oxygen-free argon (Linde 5.0) before use, and an inert gas blanket was maintained throughout the experiments. A Metrohm Autolab PGSTAT 302N potentiostat (controlled by the Autolab Nova Software) was used in cyclic voltammetric and impedance measurements. Cyclic voltammetry experiments were performed in a standard three-electrode cell arrangement in which a glassy carbon (GC) rod embedded in a glass tube (surface area $A = 0.031\ \mathrm{cm}^2$) or a gold plate ($A = 0.196\ \mathrm{cm}^2$) in contact with acetonitrile solutions containing 1 mM bis-imine based copper complex and 100 mM tetrabutylammonium tetrafluoroborate ($TBABF_4$) served as working electrode, and a platinum wire as counter electrode. An aqueous KCl-saturated calomel electrode (SCE) and the mid-point (half-wave) potential of the ferrocene/ferrocenium (Fc/Fc^+) redox couple (as an internal reference system) were used as potential references for the measurement of the electrode potentials. The aqueous electrolyte solution in the SCE and the acetonitrile solution at the working electrode were separated by a glass stopcock arrangement which effectively prevented mixing of the solutions.

Cyclic voltammetric curves in the systems containing bis-imine based copper complexes were recorded in the potential range of –1.66 V to 0.84 V *vs.* SCE at $v = 50$ mV/s sweep rate. All potentials in **Figures 2-6** are referenced simultaneously to the ferrocene/ferrocenium redox couple and to SCE. Uncompensated ohmic resistance (R_s) values (determined from impedance measurements in the high frequency range, $f > 1$ kHz [1]) varied between 20 and 30 ohms.

Results and Discussion

The $E_{1/2,Fc/Fc^+}$ value with respect to SCE was determined in acetonitrile solutions containing 100 mM the $TBABF_4$ supporting electrolyte (see **Figure 1**). The liquid junction potential was not corrected. The observed value ($E_{1/2,Fc/Fc^+} = (438 \pm 5)$ mV *vs.* SCE, see the caption in Fig.1) is in fairly good agreement with earlier results [2-4]. The R_s values (i.e. the resistance between the working electrode and the reference electrode [5]) varied between 20 and 30 ohms. Considering the magnitude of the current flowing in the electrochemical cell, it can be expected that in the case of voltammograms showed in Figs. 1a, 2a, 3-7) the influence of the IR drop on the polarization potentials is negligible (< 1.5 mV). Therefore, the cyclic voltammograms recorded at GC in contact with the electrolyte solutions are presented without IR drop corrections (Figs. 1a, 2a, 3-7). The cyclic voltammograms recorded at the gold plate were corrected with the corresponding IR drops (Figs. 1b and 2b).

As it can be seen from **Figs. 2-6**, between about –1.66 V and 0 V *vs.* SCE the shape of the cyclic voltammograms is affected primarily by the deposition-dissolution kinetics of the copper - copper ion system. The deposition of Cu during the negative going scans starts at about –0.4 V *vs.* SCE. The cyclic voltammetric curves in Figs. 2-6 show well developed peaks (p_1^-). The peak maximum values are given in **Table 1** in the potential region –0.6 V - –1.1 V *vs.* SCE followed by a distinct current plateau corresponding to the limiting current for Cu deposition. After reversing the direction of the potential scan (at –1.66 V *vs.* SCE) the electrodissolution of copper is observed in the potential range of –0.35 V to 0.05 V *vs.* SCE. The maximums of the anodic peaks (p_1^+) are between –0.23 V and –0.17 V *vs.* SCE. In some cases peaks with a shoulder (p_2^+) were observed (see Figs. 3-6 and Table 1). The charge involved in this anodic process corresponds to the electrodissolution of Cu as Cu(I) and Cu(II), yielding metal ions complexed with acetonitrile solvent molecules.

In order to prove the above conclusions, cyclic voltammetric experiments were carried out using an acetonitrile solution containing 1 mM tetrakis(acetonitrile)copper(I) hexafluorophosphate ($Cu(MeCN)_4PF_6$) and 100 mM tetrabutylammonium tetrafluoroborate ($TBABF_4$). The cyclic potential sweep was applied in the same potential range (–1.66 V to 0.84 V *vs.* SCE) and at the same sweep rate (*v* = 50 mV/s) as used for the investigation of bis-imine based copper complexes (see Fig. 7). As it can be seen in Figs. 2-7, the shapes of the cyclic voltammograms in the potential region from –1.66 V to about 0 V *vs.* SCE are very similar, and the electrode potentials corresponding to the maxima of the relevant peaks practically coincide.

In the cyclic voltammograms recorded in the presence of bis-imine based copper complexes, at potentials more positive than 0.1 V *vs.* SCE only one quasi-reversible peak couple (p_3^+ and p_3^-) can be seen in the potential range of 0.33 – 0.83 V *vs.* SCE. This quasi-reversible peak pair can be assigned to the electrochemical oxidation and reduction of the bis-imine ligands. This feature is not present in the cyclic voltammograms of the $Cu(MeCN)_4PF_6$ solutions recorded under the same conditions.

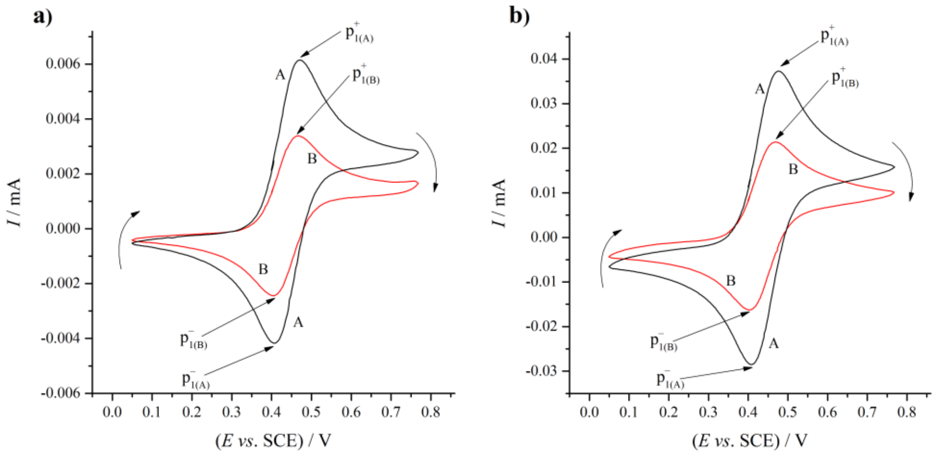


Figure 1. Cyclic voltammograms recorded at **a)** a glassy carbon (GC) rod (surface area $A = 0.031\ \mathrm{cm}^2$) and **b)** a gold plate (surface area $A = 0.196\ \mathrm{cm}^2$) in contact with (A) 0.5 mM; (B) 0.25 mM ferrocene + 100 mM $TBABF_4$ in MeCN. $v = 50\ \mathrm{mV{\cdot}s^{-1}}$; $E = 0.05 – 0.77$ V *vs.* SCE.

Peak potentials:

(*E vs.* SCE) / V	a) GC		b) Au	
0.5 mM (A)	$p^{+}_{1(A)} = 0.469$	$p^{-}_{1(A)} = 0.409$	$p^{+}_{1(A)} = 0.468$	$p^{-}_{1(A)} = 0.408$
0.25 mM (B)	$p^{+}_{1(B)} = 0.468$	$p^{-}_{1(B)} = 0.409$	$p^{+}_{1(B)} = 0.469$	$p^{-}_{1(B)} = 0.407$

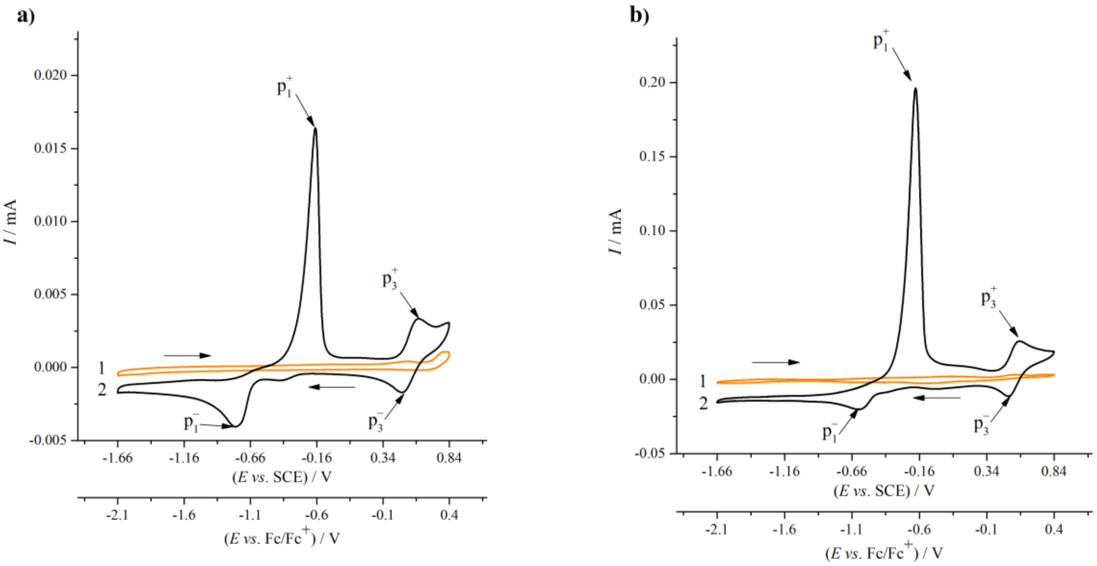


Figure 2. Cyclic voltammograms recorded at **a)** GC (surface area $A = 0.031$ cm^2) and **b)** Au (surface area $A = 0.196$ cm^2) in contact with (1) 100 mM TBABF$_4$ in MeCN and (2) 1 mM $C_{36}H_{40}CuF_6N_4O_4P$ (**6d**) + 100 mM TBABF$_4$ in MeCN. Scan rate: $v = 50$ mV·s^{-1}.

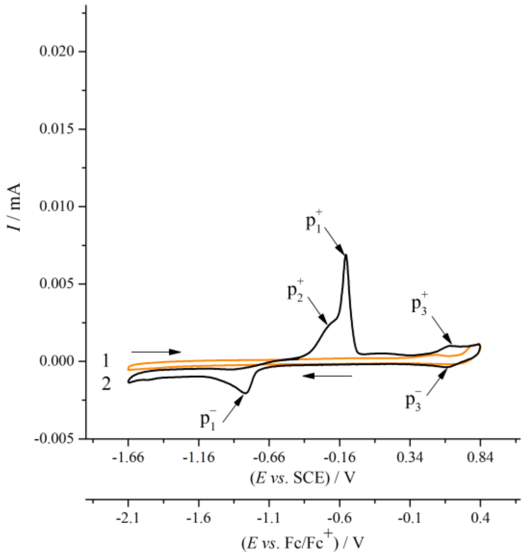


Figure 3. Cyclic voltammograms recorded at GC (surface area $A = 0.031$ cm^2) in contact with (1) 100 mM TBABF$_4$ in MeCN and (2) 1 mM $C_{32}H_{28}Br_4CuF_6N_4P$ (**6m**) + 100 mM TBABF$_4$ in MeCN. Scan rate: $v = 50$ mV·s^{-1}.

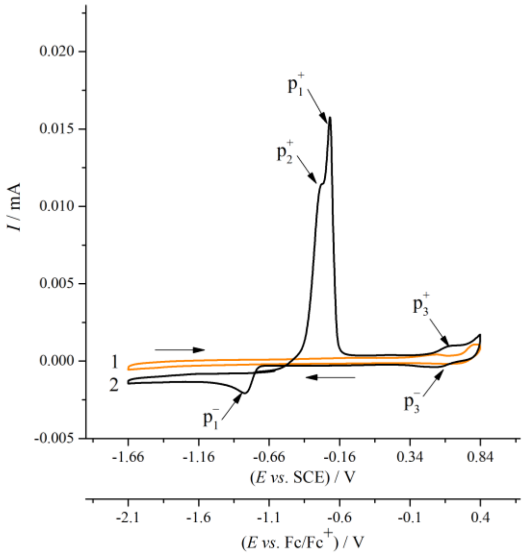


Figure 4. Cyclic voltammograms recorded at GC (surface area $A = 0.031$ cm^2) in contact with (1) 100 mM TBABF$_4$ in MeCN and (2) 1 mM $C_{32}H_{28}CuF_{10}N_4P$ (**6n**) + 100 mM TBABF$_4$ in MeCN. Scan rate: $v = 50$ mV·s^{-1}.

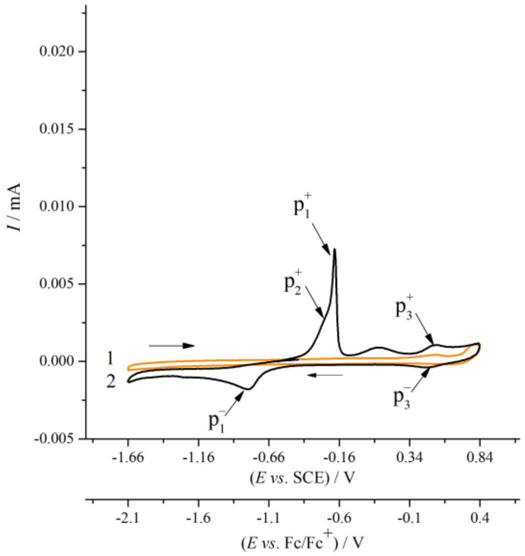


Figure 5. Cyclic voltammograms recorded at GC (surface area $A = 0.031$ cm^2) in contact with (1) 100 mM $TBABF_4$ in MeCN and (2) 1 mM $C_{32}H_{24}Cl_8CuF_6N_4P$ (**6j**) + 100 mM $TBABF_4$ in MeCN. Scan rate: $v = 50$ mV·s^{-1}.

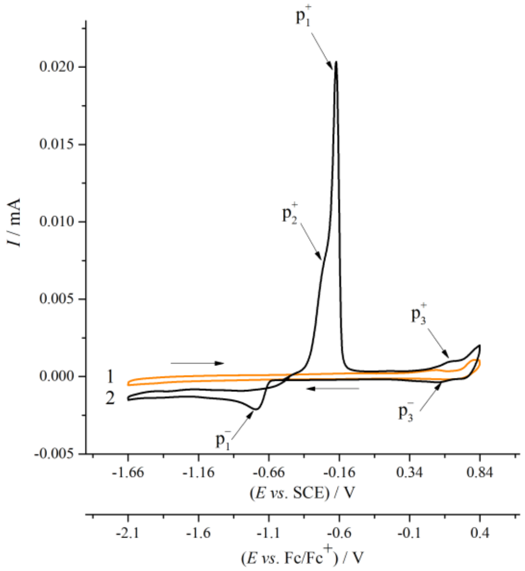


Figure 6. Cyclic voltammograms recorded at GC (surface area $A = 0.031$ cm^2) in contact with (1) 100 mM $TBABF_4$ in MeCN and (2) 1 mM $C_{32}H_{32}CuF_6N_4P$ (**6a**) + 100 mM $TBABF_4$ in MeCN. Scan rate: $v = 50$ mV·s^{-1}.

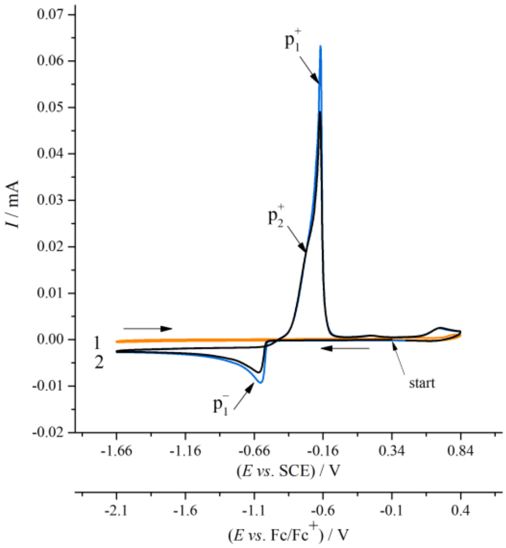


Figure 7. Cyclic voltammograms recorded at GC (surface area $A = 0.031\ \text{cm}^2$) in contact with (1) 100 mM $TBABF_4$ in MeCN and (2) 1 mM $Cu(MeCN)_4PF_6$ + 100 mM $TBABF_4$ in MeCN. Scan rate: $v = 50\ \text{mV}\cdot\text{s}^{-1}$. The black line is the first cycle, and the blue line is the second cycle, respectively. The potential scan was started from 0.34 V *vs.* SCE in the negative direction.

Table 1. The measured peak potentials (the uncertainty of the values is ±0.005 V).

E / V *vs.* SCE		p_1^+	p_1^-	p_2^+	p_3^+	p_3^-
6d	WE: GC	–0.176	–0.775		0.609	0.481
	WE: Au	–0.189	–0.616		0.583	0.502
6m	WE: GC	–0.114	–0.828	–0.227	0.627	0.597
6n	WE: GC	–0.229	–0.834	–0.288	0.646	0.544
6j	WE: GC	–0.194	–0.805	–0.257	0.526	0.463
6a	WE: GC	–0.182	–0.754	–0.266	0.626	0.557
$Cu(MeCN)_4PF_6$	WE: GC	–0.183	–0.624	–0.286		

References

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Chrystallographic Details

Crystal data, data collection and structure refinement details are summarized in Table 1.

Experimental details

Crystal data	
Chemical formula	$C_{32}H_{28}Br_4CuN_4 \cdot F_6P$
M_r	996.73
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	298
a, b, c (Å)	8.2994 (7), 23.795 (2), 18.3273 (12)
β (°)	93.367 (3)
V (Å^3)	3613.1 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.13
Crystal size (mm)	0.59 × 0.16 × 0.10
Data collection	
Diffractometer	Bruker D8 VENTURE
Absorption correction	Numerical *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
$T_{\min}$, $T_{\max}$	0.377, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	53592, 6586, 4230
R_{int}	0.160
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.605
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.087, 0.190, 1.18
No. of reflections	6586
No. of parameters	434
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{\max}$, $\Delta\rangle_{\min}$ (e Å^{-3})	1.27, -0.67

Data collection: Bruker Instrument Service vV6.2.6; cell refinement: *APEX3* v2017.3-0 (Bruker AXS); data reduction: *SAINT* V8.38A (Bruker AXS Inc., 2017); program(s) used to solve structure: SHELXT 2014/5 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2016*/6 (Sheldrick, 2016); molecular graphics: *Mercury*; software used to prepare material for publication: *WinGX*, *publCIF*.

Crystal data

$C_{32}H_{28}Br_4CuN_4 \cdot F_6P$	$F(000) = 1944$
$M_r = 996.73$	$D_x = 1.832$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.2994$ (7) Å	Cell parameters from 1614 reflections
$b = 23.795$ (2) Å	$\theta = 1.7$–$21.7°$
$c = 18.3273$ (12) Å	$\mu = 5.13$ mm^{-1}
$\beta = 93.367$ (3)°	$T = 298$ K
$V = 3613.1$ (5) Å^3	Prism, colourless
$Z = 4$	0.59 × 0.16 × 0.10 mm

Data collection

Bruker D8 VENTURE diffractometer	6586 independent reflections
Radiation source: microfocus sealed tube, INCOATEC IμS 3.0	4230 reflections with $I > 2\sigma(I)$
Multilayer mirror monochromator	$R_{\text{int}} = 0.160$
Detector resolution: 7.3910 pixels mm^{-1}	$\theta_{\text{max}} = 25.5°$, $\theta_{\text{min}} = 2.2°$
ω and π scan	$h = -10 \rightarrow 10$
Absorption correction: numerical *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction	$k = -28 \rightarrow 28$
$T_{\text{min}} = 0.377$, $T_{\text{max}} = 0.745$	$l = -19 \rightarrow 22$
53592 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.087$	H-atom parameters constrained
$wR(F^2) = 0.190$	$w = 1/[\sigma^2(F_o^2) + (0.0705P)^2 + 5.8845P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.18$	$(\Delta/\sigma)_{\text{max}} < 0.001$

6586 reflections	$\Delta\rangle_{\mathrm{max}}$ = 1.27 e Å^{-3}
434 parameters	$\Delta\rangle_{\mathrm{min}}$ = -0.67 e Å^{-3}
0 restraints	Extinction correction: *SHELXL2016*/6 (Sheldrick 2016)
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0023 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (6m)

	x	*y*	*z*	U_{iso}*/U_{eq}
C2	0.2785 (10)	0.2903 (3)	0.5482 (4)	0.0409 (18)
H2A	0.354171	0.292234	0.590489	0.049*
H2B	0.181219	0.271799	0.562688	0.049*
C3	0.2387 (10)	0.3486 (3)	0.5211 (4)	0.0419 (19)
H3A	0.177268	0.368257	0.556618	0.05*
H3B	0.337488	0.369377	0.51496	0.05*
C6	0.1417 (14)	0.2288 (4)	0.2558 (4)	0.074 (3)
H6A	0.050129	0.251891	0.239688	0.088*
H6B	0.137003	0.19422	0.227707	0.088*
C7	0.2932 (14)	0.2589 (4)	0.2434 (4)	0.070 (3)
H7A	0.383209	0.232892	0.248469	0.084*
H7B	0.288626	0.273782	0.194035	0.084*
C10	0.4474 (10)	0.2189 (3)	0.5093 (4)	0.0436 (19)
H10	0.469796	0.212153	0.558848	0.052*
C11	0.5260 (9)	0.1843 (3)	0.4559 (4)	0.0419 (19)
C12	0.5574 (10)	0.1275 (3)	0.4677 (4)	0.048 (2)
C13	0.6308 (12)	0.0949 (4)	0.4164 (6)	0.065 (3)
H13	0.649784	0.056913	0.424881	0.078*
C14	0.6746 (12)	0.1195 (4)	0.3535 (5)	0.068 (3)
H14	0.723871	0.097892	0.318863	0.082*
C15	0.6473 (12)	0.1758 (4)	0.3403 (5)	0.065 (3)
H15	0.679506	0.192331	0.297617	0.079*
C16	0.5726 (11)	0.2067 (4)	0.3907 (5)	0.056 (2)
H16	0.551907	0.244473	0.381023	0.067*

C40	0.0466 (10)	0.3847 (3)	0.4350 (4)	0.048 (2)
H40	0.037278	0.414007	0.468065	0.057*
C41	-0.0512 (9)	0.3863 (3)	0.3671 (4)	0.0437 (19)
C42	-0.0966 (11)	0.4371 (4)	0.3333 (5)	0.058 (2)
C43	-0.1895 (13)	0.4384 (6)	0.2688 (6)	0.079 (3)
H43	-0.215694	0.47265	0.246621	0.095*
C44	-0.2429 (12)	0.3898 (6)	0.2376 (6)	0.075 (3)
H44	-0.306902	0.390638	0.194194	0.091*
C45	-0.2021 (12)	0.3387 (5)	0.2702 (6)	0.077 (3)
H45	-0.238075	0.30521	0.248861	0.093*
C46	-0.1100 (11)	0.3383 (4)	0.3331 (5)	0.062 (2)
H46	-0.084826	0.303751	0.354678	0.074*
C50	0.0846 (11)	0.1673 (4)	0.3517 (4)	0.056 (2)
H50	0.063363	0.141417	0.31435	0.067*
C51	0.0590 (10)	0.1498 (3)	0.4254 (4)	0.048 (2)
C52	0.0877 (11)	0.0960 (3)	0.4504 (5)	0.053 (2)
C53	0.0559 (12)	0.0789 (4)	0.5198 (5)	0.061 (2)
H53	0.078687	0.042231	0.534722	0.074*
C54	-0.0094 (11)	0.1161 (4)	0.5667 (5)	0.064 (3)
H54	-0.033135	0.10486	0.613448	0.076*
C55	-0.0395 (11)	0.1702 (4)	0.5437 (5)	0.061 (2)
H55	-0.084102	0.19568	0.57533	0.073*
C56	-0.0048 (11)	0.1873 (4)	0.4751 (5)	0.056 (2)
H56	-0.023886	0.224365	0.461166	0.067*
C80	0.3566 (11)	0.3527 (3)	0.2709 (4)	0.052 (2)
H80	0.354767	0.356709	0.220344	0.062*
C81	0.4031 (10)	0.4012 (3)	0.3156 (4)	0.045 (2)
C82	0.3702 (11)	0.4560 (3)	0.2925 (4)	0.048 (2)
C83	0.4231 (13)	0.5015 (4)	0.3325 (5)	0.065 (3)
H83	0.398339	0.537663	0.316151	0.078*
C84	0.5119 (12)	0.4936 (4)	0.3961 (5)	0.065 (3)
H84	0.549359	0.524493	0.423155	0.078*
C85	0.5468 (11)	0.4405 (4)	0.4208 (5)	0.059 (2)
H85	0.608513	0.435527	0.464351	0.071*
C86	0.4915 (10)	0.3946 (3)	0.3818 (4)	0.047 (2)
H86	0.513327	0.358639	0.399756	0.057*
N1	0.3493 (7)	0.2580 (3)	0.4900 (3)	0.0346 (14)
N4	0.1446 (8)	0.3451 (3)	0.4514 (3)	0.0390 (15)
N5	0.1343 (9)	0.2159 (3)	0.3340 (3)	0.0487 (17)
N8	0.3184 (9)	0.3052 (3)	0.2962 (3)	0.0488 (17)

F1	0.8208 (10)	0.3882 (3)	0.5750 (4)	0.110 (2)
F2	0.8157 (9)	0.3577 (3)	0.6880 (3)	0.112 (2)
F3	0.9246 (8)	0.3059 (4)	0.6033 (5)	0.131 (3)
F4	0.6908 (10)	0.2788 (3)	0.6464 (4)	0.115 (2)
F5	0.5929 (8)	0.3622 (3)	0.6209 (6)	0.146 (4)
F6	0.6978 (11)	0.3107 (4)	0.5357 (4)	0.134 (3)
P1	0.7576 (3)	0.33353 (10)	0.61172 (12)	0.0511 (6)
Cu1	0.23599 (12)	0.28059 (4)	0.39330 (4)	0.0410 (3)
Br12	0.49469 (13)	0.09209 (4)	0.55419 (5)	0.0673 (3)
Br42	-0.02045 (15)	0.50611 (4)	0.37390 (7)	0.0851 (4)
Br52	0.17745 (18)	0.04191 (4)	0.38813 (7)	0.0906 (4)
Br82	0.24754 (16)	0.46818 (5)	0.20364 (6)	0.0821 (4)

Atomic displacement parameters (Å^{2}) for (6m)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.043 (5)	0.045 (4)	0.035 (4)	0.004 (4)	0.009 (3)	0.001 (3)
C3	0.041 (5)	0.047 (5)	0.037 (4)	0.004 (4)	0.004 (4)	-0.009 (3)
C6	0.120 (9)	0.069 (6)	0.031 (4)	-0.022 (6)	0.002 (5)	-0.007 (4)
C7	0.119 (9)	0.055 (6)	0.038 (4)	-0.014 (6)	0.023 (5)	-0.010 (4)
C10	0.043 (5)	0.043 (5)	0.045 (4)	0.002 (4)	0.001 (4)	0.007 (4)
C11	0.033 (5)	0.044 (5)	0.048 (4)	0.012 (4)	-0.004 (4)	-0.001 (4)
C12	0.036 (5)	0.052 (5)	0.054 (5)	-0.001 (4)	-0.003 (4)	0.002 (4)
C13	0.062 (7)	0.046 (5)	0.087 (7)	0.003 (5)	0.007 (6)	-0.015 (5)
C14	0.074 (7)	0.064 (6)	0.068 (6)	0.014 (5)	0.020 (5)	-0.021 (5)
C15	0.072 (7)	0.063 (6)	0.064 (6)	0.019 (5)	0.022 (5)	-0.001 (5)
C16	0.065 (6)	0.046 (5)	0.058 (5)	0.019 (4)	0.021 (5)	0.007 (4)
C40	0.053 (6)	0.042 (5)	0.049 (5)	0.008 (4)	0.008 (4)	-0.005 (4)
C41	0.037 (5)	0.052 (5)	0.042 (4)	0.012 (4)	0.007 (4)	0.000 (4)
C42	0.045 (6)	0.068 (6)	0.061 (5)	0.009 (5)	0.012 (5)	0.012 (5)
C43	0.059 (7)	0.114 (10)	0.066 (6)	0.006 (7)	0.010 (6)	0.049 (7)
C44	0.047 (7)	0.122 (10)	0.057 (6)	0.005 (7)	-0.001 (5)	0.003 (7)
C45	0.055 (7)	0.110 (9)	0.066 (6)	0.018 (6)	-0.004 (5)	-0.023 (6)
C46	0.058 (6)	0.060 (6)	0.067 (6)	0.011 (5)	-0.002 (5)	-0.007 (5)
C50	0.068 (7)	0.051 (5)	0.048 (5)	-0.017 (5)	0.002 (4)	-0.008 (4)
C51	0.041 (5)	0.049 (5)	0.054 (5)	-0.018 (4)	0.003 (4)	-0.001 (4)
C52	0.058 (6)	0.045 (5)	0.055 (5)	-0.014 (4)	0.001 (4)	-0.005 (4)
C53	0.066 (7)	0.045 (5)	0.073 (6)	-0.007 (5)	0.000 (5)	0.016 (5)
C54	0.062 (7)	0.071 (7)	0.060 (6)	-0.010 (5)	0.014 (5)	0.011 (5)
C55	0.057 (6)	0.064 (6)	0.064 (6)	-0.008 (5)	0.018 (5)	-0.009 (5)
C56	0.062 (6)	0.040 (5)	0.066 (6)	-0.003 (4)	0.007 (5)	-0.003 (4)

C80	0.070 (6)	0.054 (5)	0.032 (4)	-0.001 (5)	0.015 (4)	-0.003 (4)
C81	0.058 (6)	0.040 (4)	0.039 (4)	-0.004 (4)	0.021 (4)	-0.002 (3)
C82	0.060 (6)	0.040 (5)	0.044 (4)	-0.001 (4)	0.013 (4)	0.005 (4)
C83	0.097 (8)	0.043 (5)	0.057 (6)	0.002 (5)	0.016 (5)	-0.004 (4)
C84	0.069 (7)	0.058 (6)	0.068 (6)	-0.012 (5)	0.018 (5)	-0.025 (5)
C85	0.060 (6)	0.070 (6)	0.047 (5)	-0.001 (5)	0.008 (4)	-0.011 (5)
C86	0.056 (6)	0.043 (5)	0.044 (4)	0.002 (4)	0.017 (4)	0.005 (4)
N1	0.028 (4)	0.041 (3)	0.035 (3)	0.001 (3)	0.002 (3)	-0.002 (3)
N4	0.042 (4)	0.042 (4)	0.034 (3)	0.005 (3)	0.008 (3)	0.000 (3)
N5	0.061 (5)	0.049 (4)	0.037 (3)	-0.014 (4)	0.005 (3)	0.000 (3)
N8	0.077 (5)	0.040 (4)	0.031 (3)	-0.006 (4)	0.017 (3)	-0.006 (3)
F1	0.150 (7)	0.081 (4)	0.100 (5)	-0.050 (4)	0.007 (4)	0.005 (4)
F2	0.128 (6)	0.147 (6)	0.062 (4)	-0.033 (5)	0.005 (4)	-0.021 (4)
F3	0.070 (5)	0.148 (7)	0.178 (8)	0.033 (5)	0.026 (5)	-0.025 (6)
F4	0.149 (7)	0.075 (4)	0.123 (6)	-0.025 (4)	0.031 (5)	0.025 (4)
F5	0.065 (5)	0.102 (5)	0.270 (11)	0.022 (4)	-0.003 (5)	-0.036 (6)
F6	0.174 (8)	0.143 (7)	0.081 (5)	-0.060 (6)	-0.021 (5)	-0.025 (4)
P1	0.0443 (14)	0.0524 (14)	0.0565 (13)	0.0017 (11)	0.0019 (11)	-0.0040 (10)
Cu1	0.0532 (7)	0.0400 (5)	0.0302 (5)	0.0018 (5)	0.0055 (4)	-0.0032 (4)
Br12	0.0802 (8)	0.0574 (6)	0.0636 (6)	-0.0027 (5)	-0.0029 (5)	0.0120 (4)
Br42	0.0883 (9)	0.0544 (6)	0.1132 (9)	0.0038 (6)	0.0117 (7)	0.0165 (6)
Br52	0.1278 (11)	0.0540 (6)	0.0923 (8)	0.0006 (6)	0.0249 (7)	-0.0201 (6)
Br82	0.1173 (10)	0.0675 (7)	0.0599 (6)	-0.0015 (6)	-0.0081 (6)	0.0157 (5)

Geometric parameters (Å, º) for (6m)

C2—N1	1.464 (9)	C45—H45	0.93
C2—C3	1.503 (10)	C46—H46	0.93
C2—H2A	0.97	C50—N5	1.275 (10)
C2—H2B	0.97	C50—C51	1.443 (11)
C3—N4	1.460 (9)	C50—H50	0.93
C3—H3A	0.97	C51—C52	1.376 (11)
C3—H3B	0.97	C51—C56	1.399 (12)
C6—N5	1.471 (10)	C52—C53	1.375 (12)
C6—C7	1.476 (14)	C52—Br52	1.901 (9)
C6—H6A	0.97	C53—C54	1.368 (13)
C6—H6B	0.97	C53—H53	0.93
C7—N8	1.475 (10)	C54—C55	1.373 (13)
C7—H7A	0.97	C54—H54	0.93
C7—H7B	0.97	C55—C56	1.369 (12)
C10—N1	1.273 (9)	C55—H55	0.93

C10—C11	1.461 (11)	C56—H56	0.93
C10—H10	0.93	C80—N8	1.268 (10)
C11—C16	1.384 (11)	C80—C81	1.454 (11)
C11—C12	1.392 (11)	C80—H80	0.93
C12—C13	1.385 (12)	C81—C86	1.389 (11)
C12—Br12	1.895 (8)	C81—C82	1.394 (10)
C13—C14	1.361 (13)	C82—C83	1.365 (12)
C13—H13	0.93	C82—Br82	1.891 (8)
C14—C15	1.377 (13)	C83—C84	1.356 (13)
C14—H14	0.93	C83—H83	0.93
C15—C16	1.359 (11)	C84—C85	1.367 (13)
C15—H15	0.93	C84—H84	0.93
C16—H16	0.93	C85—C86	1.371 (12)
C40—N4	1.270 (10)	C85—H85	0.93
C40—C41	1.446 (11)	C86—H86	0.93
C40—H40	0.93	N1—Cu1	2.030 (6)
C41—C46	1.377 (12)	N4—Cu1	2.040 (6)
C41—C42	1.400 (12)	N5—Cu1	2.038 (6)
C42—C43	1.374 (13)	N8—Cu1	2.030 (6)
C42—Br42	1.895 (10)	F1—P1	1.568 (6)
C43—C44	1.354 (15)	F2—P1	1.561 (6)
C43—H43	0.93	F3—P1	1.550 (7)
C44—C45	1.388 (15)	F4—P1	1.565 (6)
C44—H44	0.93	F5—P1	1.545 (7)
C45—C46	1.344 (13)	F6—P1	1.550 (7)
N1—C2—C3	109.5 (6)	C56—C51—C50	120.5 (8)
N1—C2—H2A	109.8	C53—C52—C51	123.0 (8)
C3—C2—H2A	109.8	C53—C52—Br52	117.3 (7)
N1—C2—H2B	109.8	C51—C52—Br52	119.7 (7)
C3—C2—H2B	109.8	C54—C53—C52	119.6 (8)
H2A—C2—H2B	108.2	C54—C53—H53	120.2
N4—C3—C2	109.4 (6)	C52—C53—H53	120.2
N4—C3—H3A	109.8	C53—C54—C55	119.1 (9)
C2—C3—H3A	109.8	C53—C54—H54	120.4
N4—C3—H3B	109.8	C55—C54—H54	120.4
C2—C3—H3B	109.8	C56—C55—C54	121.0 (9)
H3A—C3—H3B	108.2	C56—C55—H55	119.5
N5—C6—C7	109.7 (8)	C54—C55—H55	119.5
N5—C6—H6A	109.7	C55—C56—C51	121.1 (8)

C7—C6—H6A	109.7	C55—C56—H56	119.4
N5—C6—H6B	109.7	C51—C56—H56	119.4
C7—C6—H6B	109.7	N8—C80—C81	124.3 (7)
H6A—C6—H6B	108.2	N8—C80—H80	117.8
N8—C7—C6	110.6 (7)	C81—C80—H80	117.8
N8—C7—H7A	109.5	C86—C81—C82	117.1 (7)
C6—C7—H7A	109.5	C86—C81—C80	120.8 (7)
N8—C7—H7B	109.5	C82—C81—C80	122.1 (8)
C6—C7—H7B	109.5	C83—C82—C81	121.9 (8)
H7A—C7—H7B	108.1	C83—C82—Br82	118.7 (6)
N1—C10—C11	122.0 (7)	C81—C82—Br82	119.4 (6)
N1—C10—H10	119.0	C84—C83—C82	119.6 (9)
C11—C10—H10	119.0	C84—C83—H83	120.2
C16—C11—C12	116.7 (7)	C82—C83—H83	120.2
C16—C11—C10	121.3 (7)	C83—C84—C85	120.5 (9)
C12—C11—C10	122.1 (7)	C83—C84—H84	119.8
C13—C12—C11	121.6 (8)	C85—C84—H84	119.8
C13—C12—Br12	118.2 (7)	C84—C85—C86	120.4 (9)
C11—C12—Br12	120.2 (6)	C84—C85—H85	119.8
C14—C13—C12	119.0 (9)	C86—C85—H85	119.8
C14—C13—H13	120.5	C85—C86—C81	120.6 (8)
C12—C13—H13	120.5	C85—C86—H86	119.7
C13—C14—C15	121.1 (8)	C81—C86—H86	119.7
C13—C14—H14	119.5	C10—N1—C2	117.3 (6)
C15—C14—H14	119.5	C10—N1—Cu1	133.8 (5)
C16—C15—C14	119.0 (9)	C2—N1—Cu1	108.1 (4)
C16—C15—H15	120.5	C40—N4—C3	117.9 (6)
C14—C15—H15	120.5	C40—N4—Cu1	133.4 (5)
C15—C16—C11	122.7 (8)	C3—N4—Cu1	107.7 (5)
C15—C16—H16	118.7	C50—N5—C6	117.9 (7)
C11—C16—H16	118.7	C50—N5—Cu1	132.8 (6)
N4—C40—C41	122.9 (7)	C6—N5—Cu1	108.8 (5)
N4—C40—H40	118.6	C80—N8—C7	117.0 (6)
C41—C40—H40	118.6	C80—N8—Cu1	133.0 (5)
C46—C41—C42	116.0 (8)	C7—N8—Cu1	108.5 (5)
C46—C41—C40	122.3 (8)	F5—P1—F3	178.8 (5)
C42—C41—C40	121.7 (8)	F5—P1—F6	90.8 (5)
C43—C42—C41	121.5 (10)	F3—P1—F6	90.2 (5)
C43—C42—Br42	118.4 (8)	F5—P1—F2	88.2 (5)
C41—C42—Br42	120.0 (7)	F3—P1—F2	90.8 (5)

C44—C43—C42	119.8 (10)	F6—P1—F2	178.8 (5)
C44—C43—H43	120.1	F5—P1—F4	89.2 (5)
C42—C43—H43	120.1	F3—P1—F4	91.6 (5)
C43—C44—C45	120.0 (10)	F6—P1—F4	88.4 (4)
C43—C44—H44	120.0	F2—P1—F4	92.3 (4)
C45—C44—H44	120.0	F5—P1—F1	90.1 (5)
C46—C45—C44	119.3 (11)	F3—P1—F1	89.1 (5)
C46—C45—H45	120.4	F6—P1—F1	90.2 (4)
C44—C45—H45	120.4	F2—P1—F1	89.2 (4)
C45—C46—C41	123.3 (10)	F4—P1—F1	178.3 (4)
C45—C46—H46	118.3	N1—Cu1—N8	132.8 (3)
C41—C46—H46	118.3	N1—Cu1—N5	114.9 (2)
N5—C50—C51	124.6 (8)	N8—Cu1—N5	84.3 (3)
N5—C50—H50	117.7	N1—Cu1—N4	84.9 (2)
C51—C50—H50	117.7	N8—Cu1—N4	113.3 (2)
C52—C51—C56	116.2 (8)	N5—Cu1—N4	133.8 (3)
C52—C51—C50	123.3 (8)		
N1—C2—C3—N4	50.9 (8)	Br52—C52—C53—C54	-179.7 (7)
N5—C6—C7—N8	-48.0 (11)	C52—C53—C54—C55	-1.1 (14)
N1—C10—C11—C16	35.6 (12)	C53—C54—C55—C56	-0.1 (15)
N1—C10—C11—C12	-144.2 (8)	C54—C55—C56—C51	1.5 (14)
C16—C11—C12—C13	-0.4 (12)	C52—C51—C56—C55	-1.5 (13)
C10—C11—C12—C13	179.5 (8)	C50—C51—C56—C55	175.7 (8)
C16—C11—C12—Br12	-178.7 (6)	N8—C80—C81—C86	35.4 (13)
C10—C11—C12—Br12	1.1 (11)	N8—C80—C81—C82	-148.5 (9)
C11—C12—C13—C14	0.7 (14)	C86—C81—C82—C83	0.5 (12)
Br12—C12—C13—C14	179.1 (7)	C80—C81—C82—C83	-175.7 (8)
C12—C13—C14—C15	0.1 (15)	C86—C81—C82—Br82	-179.0 (6)
C13—C14—C15—C16	-1.2 (16)	C80—C81—C82—Br82	4.8 (11)
C14—C15—C16—C11	1.6 (15)	C81—C82—C83—C84	0.8 (14)

C12—C11—C16—C15	-0.9 (14)	Br82—C82—C83—C84	-179.6 (7)
C10—C11—C16—C15	179.3 (9)	C82—C83—C84—C85	-0.9 (15)
N4—C40—C41—C46	33.3 (13)	C83—C84—C85—C86	-0.5 (14)
N4—C40—C41—C42	-149.1 (8)	C84—C85—C86—C81	1.8 (13)
C46—C41—C42—C43	-2.3 (13)	C82—C81—C86—C85	-1.8 (12)
C40—C41—C42—C43	180.0 (8)	C80—C81—C86—C85	174.4 (8)
C46—C41—C42—Br42	-178.9 (6)	C11—C10—N1—C2	-179.6 (7)
C40—C41—C42—Br42	3.3 (11)	C11—C10—N1—Cu1	11.6 (12)
C41—C42—C43—C44	1.9 (15)	C3—C2—N1—C10	151.7 (7)
Br42—C42—C43—C44	178.6 (8)	C3—C2—N1—Cu1	-36.8 (7)
C42—C43—C44—C45	-0.8 (16)	C41—C40—N4—C3	179.1 (7)
C43—C44—C45—C46	0.3 (16)	C41—C40—N4—Cu1	12.2 (13)
C44—C45—C46—C41	-0.8 (16)	C2—C3—N4—C40	151.6 (7)
C42—C41—C46—C45	1.8 (14)	C2—C3—N4—Cu1	-38.4 (7)
C40—C41—C46—C45	179.5 (9)	C51—C50—N5—C6	-175.1 (9)
N5—C50—C51—C52	-145.0 (10)	C51—C50—N5—Cu1	13.5 (15)
N5—C50—C51—C56	37.9 (14)	C7—C6—N5—C50	-137.4 (9)
C56—C51—C52—C53	0.3 (13)	C7—C6—N5—Cu1	35.9 (9)
C50—C51—C52—C53	-176.8 (8)	C81—C80—N8—C7	-173.0 (9)
C56—C51—C52—Br52	-179.0 (6)	C81—C80—N8—Cu1	22.5 (14)
C50—C51—C52—Br52	3.8 (12)	C6—C7—N8—C80	-132.4 (9)
C51—C52—C53—C54	1.0 (15)	C6—C7—N8—Cu1	35.8 (9)

*Hydrogen-bond geometry (Å, º) for (*6m*)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···F5	0.97	2.62	3.332 (11)	130

C2—H2*B*···F3$^{\mathrm{i}}$	0.97	2.44	3.183 (10)	134
C43—H43···Br52$^{\mathrm{ii}}$	0.93	3.00	3.792 (9)	144

Symmetry codes: (i) *x*-1, *y*, *z*; (ii) -*x*, *y*+1/2, -*z*+1/2.

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