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"Columnar self-assembly of bowl shaped fluorescent liquid crystals based on calix[4]arene with schiff base units"

Vinay S. Sharma[a*], Anuj S.Sharma[b], Rajesh H. Vekariya[c]

[a]: *Department of Chemistry, Faculty of Basic and Applied Science, Madhav University, Sirohi, Rajasthan, India.*

[b]: *Department of Chemistry, School of Science, Gujarat University, Ahmedabad, Gujarat, India.*

[C]:*Blue ORB Solution LLC, 1100 Corporate Square Drive Suite 123, Creve Coeur, Saint Lois, MO 63132, USA.*

Email address of corresponding author*: vinaysharma3836@gmail.com

Contents:

1. Experimental

Melting points were taken on Opti-Melt (Automated melting point system). The FT-IR spectra were recorded as KBr pellet on Shimadzu in the range of 3800-600 cm^{-1}. Microanalysis was performed on Perkin-Elmer PE 2400 CHN analyser. The texture images were studied on a trinocular optical polarising microscope (POM) equipped with a heating stage. ^{1}H NMR spectra and ^{13}C NMR was recorded on a 400 MHz in Bruker Advance 400 in the range of 0.5 ppm-16 ppm using $CDCl_3$ solvent. The phase transition temperatures were measured using Shimadzu DSC-50 at heating and cooling rates of 10°C min^{-1}. The samples were heated from room temperature to 550˚C at 10˚C/min. X-ray diffraction (XRD) measurements were performed on a Rigaku-Ultima IV powder diffractometer equipped with a Cu kα source (λ = 1.5418 A˚ and 1.6 kW, X-ray tube with applied voltage and current values as 40 kV and 30 mA power) and also Philips X'PERT MPD. The absorption spectra were studied by using Jasco V-570 UV-Vis recording spectrophotometer with a variable wavelength between 200 and 800 nm. The fluorescence spectra were recorded on a Jasco FP-6500 spectrofluorometer.

2. Synthesis and characterization

2.1 Preparation of *p-tert*-butyl calix[4]arene (1d)

p-tert-Butylcalix[4]arene (1d) was synthesized by reported in the literature [1], white precipitates, yield 87%. Elemental analysis: $C_{44}H_{56}O_4$: Calcu: C, 80.44; H, 8.70; O, 9.80 %, Found: C, 80.14; H, 8.62; O, 9.72 %. ^{1}H NMR: (300 MHz, $CDCl_3$): 1.18 (s, 36H, t-butyl), 3.28, 4.21 (d, J = *12.0Hz*, 4H, Ar-CH_2-Ar), 7.14 (s, 8H, Ar-H), 9.78 (s, 4H, Ar-OH); ^{13}C NMR: 149.1, 126.2, 126.1 (Ar-C), 34.2 (t-butyl), 31.4 (t-butyl), 32.6 (Ar-CH_2-Ar).

2.2 Preparation of 4-n-alkoxy acetanilide (1a)

4-n-alkoxy acetanilide (1a) was synthesized by refluxing the mixture of 4-hydroxy acetanilide (1 equiv.) with corresponding n-alkyl bromide (R-Br) (1 equiv.) in presence of anhydrous K_2CO_3 (1 equiv.) in dry acetone as a solvent [2].

2.3 Preparation of 4-n-alkoxy aniline (1b)

4-n-alkoxy aniline was prepared by the hydrolysis method reported in literature [2].

2.4 Preparation of 4-(4-n-alkoxy phenyl) imino methyl phenol (1c)

4-(4-n-alkoxy phenyl) imino methyl phenol (1c) was prepared by the reaction of comp.1b with 4-hydroxy benzaldehyde in presence of few drops of glacial acetic acid in ethanol [3]. The ^{1}H NMR of shows singlet of 1H (δ = 8.48 ppm, -N=CH-). From FT-IR, the peak found at 1630 cm^{-1} signifying the presence of -N=CH- group.

2.5 Preparation of P-*tert*-butyl calix[4]arene tetra bromo ethanoic acid (1e)

P-*tert*-butyl calix[4]arene tetra bromo ethanoic acid is formed by reaction of p-tert butyl calix[4]arene (0.01 mmol) with bromo ethanoic acid (0.04 mmol), dicyclohexyl carbodiimide (DCC) (0.0060 mol.) and dimethylaminopyridine (DMAP) in catalytic amount (0.0030 mmol) in dry CH_2Cl_2 (DCM) (30 ml) was stirred at room temperature for 12 h. The white precipitate of DCU is obtained which was isolated by filtration. The resultant crude residue was purified by column chromatography on silica gel eluting with methanol: chloroform as eluent (1:4) [4]. From FT-IR, the peak found at 1730 cm^{-1} signifying the presence of ester group.

2.6 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra n-alkoxy phenyl imine methyl phenoxy acetate calix[4]arene (1f)

The compound has been prepared by esterification of the appropriate compound (1b) (0.0015 mol.) and compound (1c) (0.0060 mol.) in dry acetone (30 ml) with presence of anhydrous K_2CO_3 was reflux at 2 hr and then extracted with DCM. The resultant crude residue was purified by column chromatography on silica gel eluting with methanol: chloroform as eluent (1:4) [5].

2.6.1 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra dodecyloxy phenyl imine methyl phenoxy acetate calix[4]arene ($1f_{12}$): Yield 69 %, FT-IR (KBr) in cm^{-1}: 2890 (-C-H- Str in aromatic), 1365 and 1236 (-C-O str), 641 Polymethylene (-CH_2-)n of –$OC_{12}H_{25}$, 1630 (-N=CH-), 1730 (-COO- group). ^{1}H NMR: 1.31 (s, 36H, t-butyl group), 0.88-0.90 (t, 12H, -$OC_{12}H_{25}$), 1.26-1.29 (m, 73H, -$OC_{12}H_{25}$), 1.47 (p, 8H, -$OC_{12}H_{25}$), 3.61 (d, *J = 12.0Hz*, 4H, -ArCH_2Ar-), 4.04 (t, 8H, -$OC_{12}H_{25}$), 4.24 (d, *J = 12.0Hz, 4H*, -ArCH_2Ar-), 4.96 (s, 8H, -O-CH_2-), 7.84 (d, 4H, Ar-H), 7.39 (s, 4H, Ar-H), 6.83 (s, 4H, Ar-H), 7.36 (d, 4H, Ar-H), 9.61 (s, 4H, -N=CH-). ^{13}C NMR: 160.1, 147.5, 128.4, 125.8, 114.6, 129.3, 130.2 (Ar-C), 31.3 (t-butyl), 14.1, 22.7, 25.9, 29.6, 64.9, 65.7, (-CH_2), 157.9 (-N=CH-), 161.1 (-C=O), 29.3, 31.3 (-CH_3).

2.6.2 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra octyloxy phenyl imine methyl phenoxy acetate calix[4]arene ($1f_8$): Yield 69%, FT-IR (KBr) in cm^{-1}: 2950 (-C-H- Str in aromatic), 1361 and 1240 (-C-O str), 691 Polymethylene (-CH_2-)n of –OC_8H_{17}, 1630 (-N=CH-), 1740 (-COO- group). ^{1}H NMR: 1.31 (s, 36H, t-butyl group), 0.88-0.90 (t, 12H, -OC_8H_{17}), 1.26-1.37 (m, 39H, -OC_8H_{17}), 1.47 (p, 8H, -OC_8H_{17}), 3.62 (d, *J = 12.0Hz*, 4H, -ArCH_2Ar-), 4.06 (t, 8H, -OC_8H_{17}), 4.26 (d, *J = 12.0Hz, 4H*, -ArCH_2Ar-), 5.21 (s, 8H, -O-CH_2-), 7.84 (d, *J = 8.2Hz*, 4H, Ar-H), 7.01 (s, 4H, Ar-H), 7.14 (s, Ar-H), 6.87 (s, *J = 8.4Hz*, 4H, Ar-H), 7.32 (d, 4H, Ar-H), 8.71 (s, 4H, -N=CH-). ^{13}C NMR: 160.4, 147.5, 127.6, 128.7, 114.6 (Ar-C), 32.5 (t-butyl), 14.1, 22.7, 25.9, 29.6, 65.8 (-CH_2), 157.9 (-N=CH-), 161.1 (-C=O), 31.9 (-CH_3).

2.6.3 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra hexyloxy phenyl imine methyl phenoxy acetate calix[4]arene ($1f_6$): Yield 71 %, FT-IR (KBr) in cm^{-1}: 2980 (-C-H- Str in aromatic), 1361 and 1244 (-C-O str), 723 Polymethylene (-CH_2-)n of –OC_6H_{13}, 1640 (-N=CH-), 1760 (-COO- group). ^{1}H NMR: 1.31 (s, 36H, t-butyl group), 0.88-0.90 (t, 12H, -OC_6H_{13}), 1.26-1.37 (m, 36H, -OC_6H_{13}), 1.47 (p, 8H, -OC_6H_{13}), 3.62 (d, *J = 12.0Hz*, 4H, -ArCH_2Ar-), 4.06(t, 8H, -OC_6H_{13}), 4.21 (d, *J = 12.0Hz*, 4H, -ArCH_2Ar-), 5.21 (s, -OCH_2-), 7.14 (s, 8H, Ar-H), 7.84 (d, 4H, Ar-H), 7.01 (s, 4H, Ar-H), 6.87 (s, *J = 8,4Hz*, 4H, Ar-H), 7.32 (d, *J = 8 Hz*, 4H, Ar-H), 8.78 (s, 4H, -N=CH-). ^{13}C NMR: 160.2, 147.6, 127.6, 128.7, 114.4 (Ar-C), 32.5 (t-butyl), 14.1, 22.7, 29.6, 25.9, 64.9 (-CH_2), 157.9 (-N=CH-), 160.4 (-C=O), 31.3 (-CH_3).

2.6.4 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra butyloxy phenyl imine methyl phenoxy acetate calix[4]arene ($1f_4$): Yield 73 %, FT-IR (KBr) in cm^{-1}: 2980 (-C-H- Str in aromatic), 1361 and 1241 (-C-O str), 821 Polymethylene (-CH_2-)n of –OC_4H_9, 1630 (-N=CH-),1760 (-COO- group). ^{1}H NMR: 1.31 (s, 36H, t-butyl group), 0.88-0.90 (t, 12H, -OC_4H_9), 1.73 (sext, 8H, -OC_4H_9), 1.47 (p, 8H, -OC_4H_9), 3.61 (d, *J = 12.0Hz, 4H*, -ArCH_2Ar-), 4.06(t, 8H, -OC_4H_9), 4.26 (d, *J = 12.0Hz, 4H*, -ArCH_2Ar-), 5.21 (s, 8H, -OC_4H_9), 7.14 (s, 8H, Ar-H), 7.84 (d, 4H, Ar-H), 7.01 (s, 4H, Ar-H), 6.87 (s, *J = 8,4Hz*, 4H, Ar-H), 7.32 (d, *J = 8 Hz*, 4H, Ar-H), 8.75 (s, 4H, -N=CH-). ^{13}C NMR: 160.4, 147.5, 127.6, 128.7, 114.4, 115.7 (Ar-C), 32.5 (t-butyl), 14.1, 19.1, 31.3, 34.5, 65.4 (-CH_2), 157.9 (-N=CH-), 160.4 (-C=O), 31.3 (-CH_3).

2.6.5 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra decyloxy phenyl imine methyl phenoxy acetate calix[4]arene ($1f_{10}$): Yield 65 %, FT-IR (KBr) in cm^{-1}: 2896 (-C-H- Str in aromatic), 1369 and 1236 (-C-O str), 764 Polymethylene (-CH_2-)n of –$OC_{10}H_{21}$, 1630 (-N=CH-), 1730 (-COO- group). ^{1}H NMR: 1.31 (s, 36H, t-butyl group), 0.88-0.90 (t, 12H, -$OC_{10}H_{21}$), 1.26-1.29 (m, 53H, -$OC_{10}H_{21}$), 1.47 (p, 8H, -$OC_{10}H_{21}$), 3.61 (d, *J = 12.0Hz*, 4H, -

$ArCH_2Ar$-), 4.21 (d, *J = 12.0Hz, 4H*, -$ArCH_2Ar$-), 4.04 (t, 8H, -$OC_{10}H_{21}$), 5.21 (s, 8H, -O-CH_2-), 7.14 (s, 8H, Ar-H), 7.84 (d, 4H, Ar-H), 7.39 (d, 4H, Ar-H), 6.83 (d, *J = 8.8 Hz*, 4H, Ar-H), 7.36 (d, *J = 8 Hz*, 4H, Ar-H), 8.41 (s, 4H, -N=CH-). ^{13}C NMR: 160.1, 147.5, 128.4, 125.8, 114.6 (Ar-C), 31.3 (t-butyl), 14.1, 22.7, 25.9, 29.6, 65.7 (-CH_2), 157.9 (-N=CH-), 161.1 (-C=O), 32.5 (-CH_3).

2.6.6 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra tetradecyloxy phenyl imine methyl phenoxy acetate calix[4]arene ($1f_{14}$): Yield 65 %, FT-IR (KBr) in cm^{-1}: 2890 (-C-H- Str in aromatic), 1365 and 1236 (-C-O str), 641 Polymethylene (-CH_2-)n of –$OC_{14}H_{29}$, 1630 (-N=CH-), 1730 (-COO- group). ^{1}H NMR: 1.31 (s, 36H, t-butyl group), 0.88 (t, 12H, -$OC_{14}H_{29}$), 1.26-1.29 (m, 81H, -$OC_{14}H_{29}$), 1.47 (p, 8H, -$OC_{14}H_{29}$), 3.61 (d, *J = 12.0Hz*, 4H, -$ArCH_2Ar$-), 4.04 (t, 8H, -$OC_{14}H_{29}$), 4.24 (d, *J = 12.0Hz, 4H*, -$ArCH_2Ar$-), 5.22 (s, 8H, -O-CH_2-), 7.13 (s, 8H, Ar-H), 7.92 (d, *J = 7.8 Hz*, 4H, Ar-H), 7.37 (d, 4H, Ar-H), 6.96 (d, *J = 8.2 Hz*, 4H, Ar-H), 7.90 (d, *J = 8Hz*, 4H, Ar-H), 8.74 (s, 4H, -N=CH-).^{13}C NMR: 160.1, 147.5, 128.4, 125.8, 114.6 (Ar-C), 32.6 (t-butyl), 14.1, 22.7, 25.9, 29.6, 64.9, 65.7 (-CH_2), 157.9 (-N=CH-), 161.1 (-C=O), 31.3 (-CH_3).

2.6.7 Preparation of 5, 11, 17, 23-tetra-t-butyl-25, 26, 27, 28 tetra hexadecyloxy phenyl imine methyl phenoxy acetate calix[4]arene ($1f_{16}$): Yield 65 %, FT-IR (KBr) in cm^{-1}: 2890 (-C-H- Str in aromatic), 1363 and 1230 (-C-O str), 640 Polymethylene (-CH_2-)n of –$OC_{16}H_{33}$, 1630 (-N=CH-), 1730 (-COO- group). ^{1}H NMR: 1.31 (s, 36H, t-butyl group), 0.88 (t, 12H, -$OC_{16}H_{33}$), 1.26-1.29 (m, 92H, -$OC_{16}H_{33}$), 1.47 (p, 8H, -$OC_{16}H_{33}$), 3.62 (d, *J = 12.0Hz*, 4H, -$ArCH_2Ar$-), 4.04 (t, 8H, -$OC_{16}H_{33}$), 4.26 (d, *J = 12.0Hz*, 4H, -ArCH2Ar-), 5.22 (s, 8H, -O-CH_2-), 7.13 (s, 8H, Ar-H), 7.92 (d, *J = 7.8 Hz*, 4H, Ar-H), 7.37 (d, 4H, Ar-H), 6.96 (d, *J = 8.2Hz*, 4H, Ar-H), 7.90 (d, *J = 8Hz*, 4H, Ar-H), 8.74 (s, 4H, -N=CH-). ^{13}C NMR: 160.1, 147.5, 143.6, 128.4,

125.8, 114.6 (Ar-C), 31.3 (t-butyl), 14.1, 22.7, 25.9, 29.6, 65.7 (-CH_2), 157.9 (-N=CH-), 161.1 (-C=O), 32.5 (-CH_3).

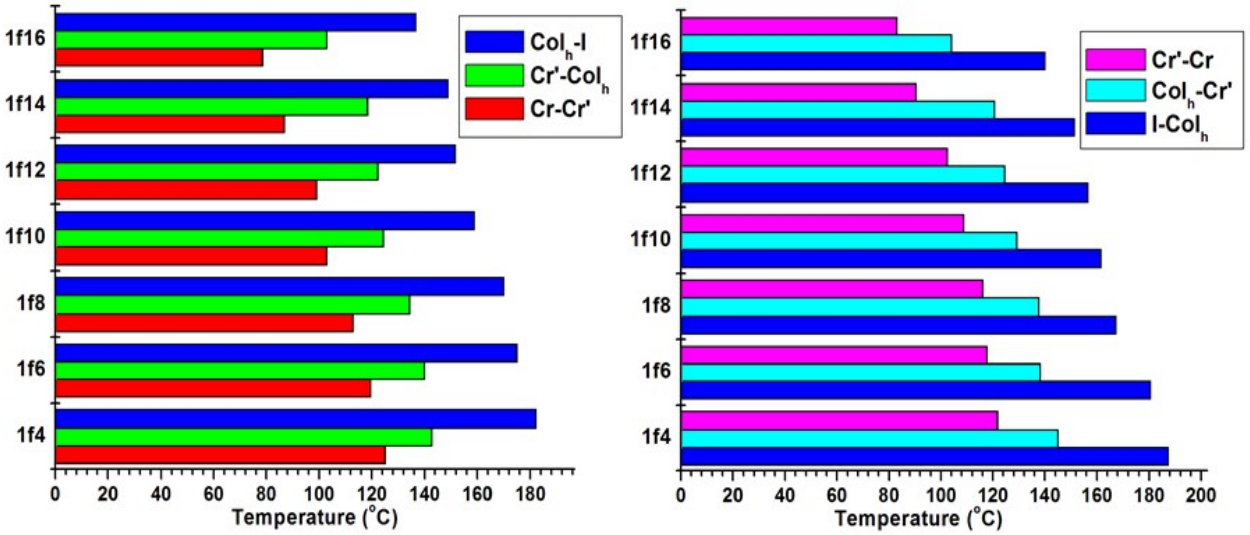

Figure S_1: Bargraph showing the thermal behaviour of compounds $1f_4$-$1f_{16}$ (heating and cooling cycle).

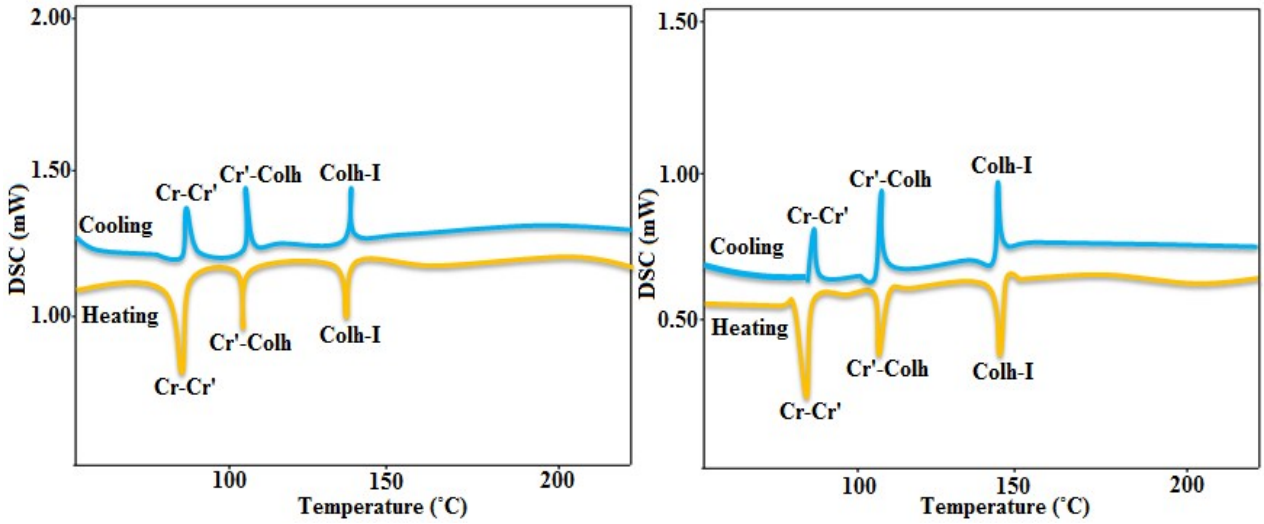

Figure S_2: The DSC traces of compounds $1f_{16}$ (a), $1f_{14}$ (b) on first heating and cooling (scan rate 10˚C/min).

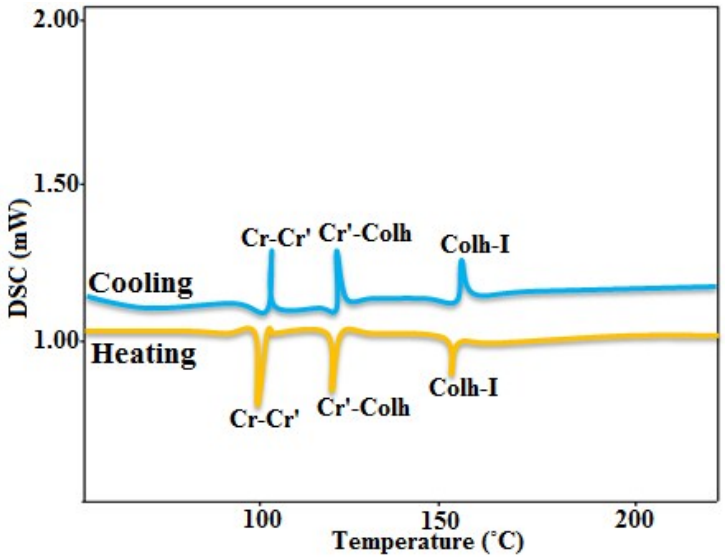

Figure S_3: The DSC traces of compounds $1f_{12}$ on first heating and cooling (scan rate 10˚C/min).

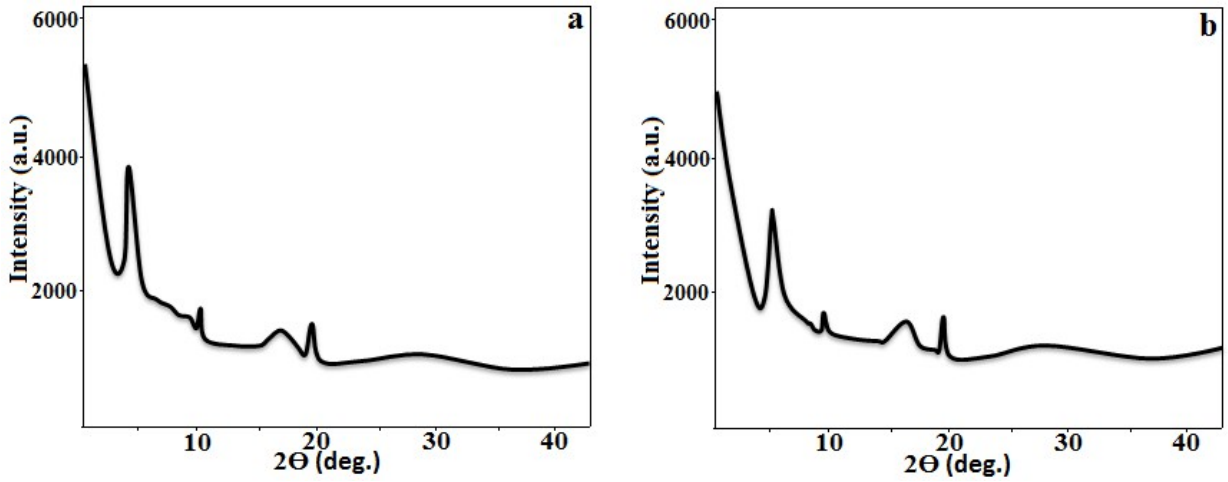

Figure S_4: XRD profiles depicting the intensity against the 2Θ obtained for the Colh phase of compound $1f_8$ at 126.0 ˚C (a); Colh phase of compound $1f_{10}$ at122.0 ˚C (b) on cooling from isotropic temperature.

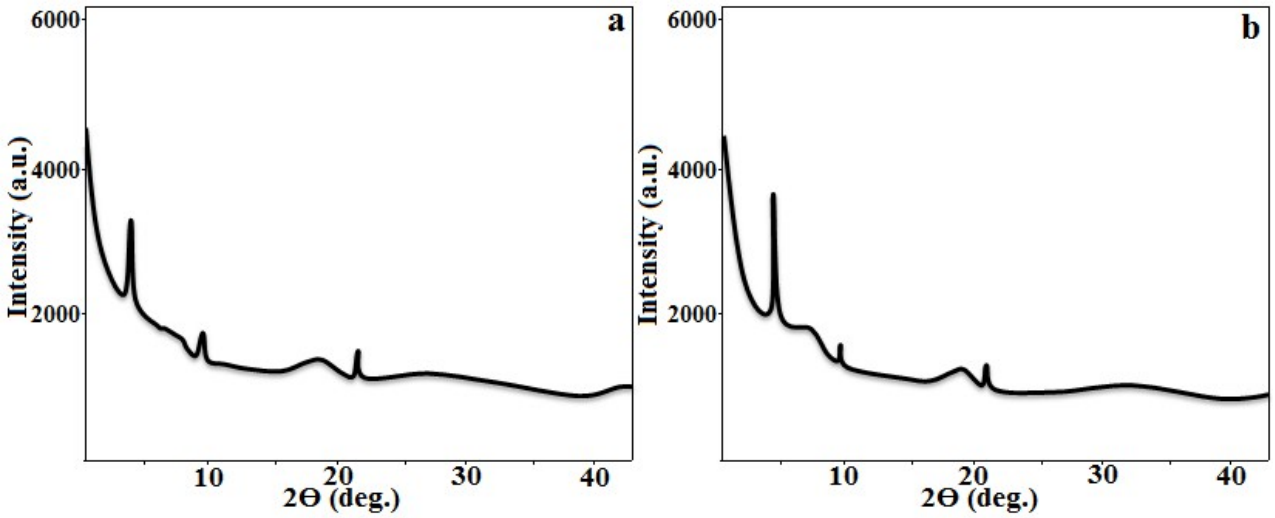

Figure S_5: XRD profiles depicting the intensity against the 2Θ obtained for the Colh phase of compound $1f_{12}$ at 122.0 ˚C (a); Colh phase of compound $1f_{14}$ at 117.0 ˚C (b) on cooling from isotropic temperature.

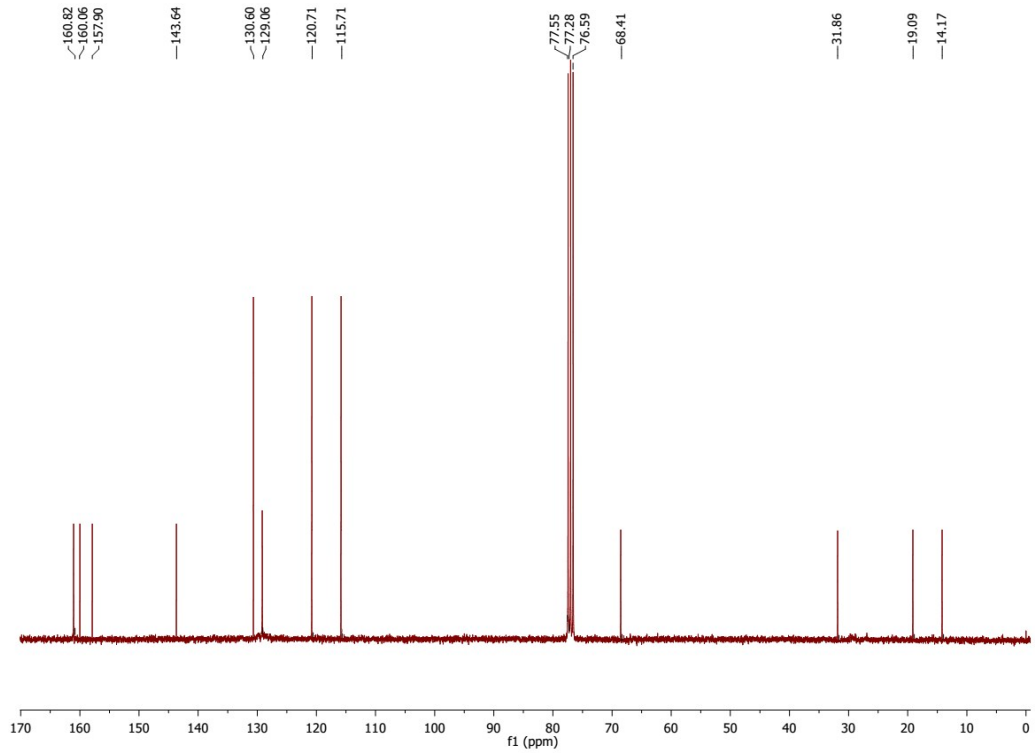

Figure S_6: ^{13}C NMR of compound $1C_4$.

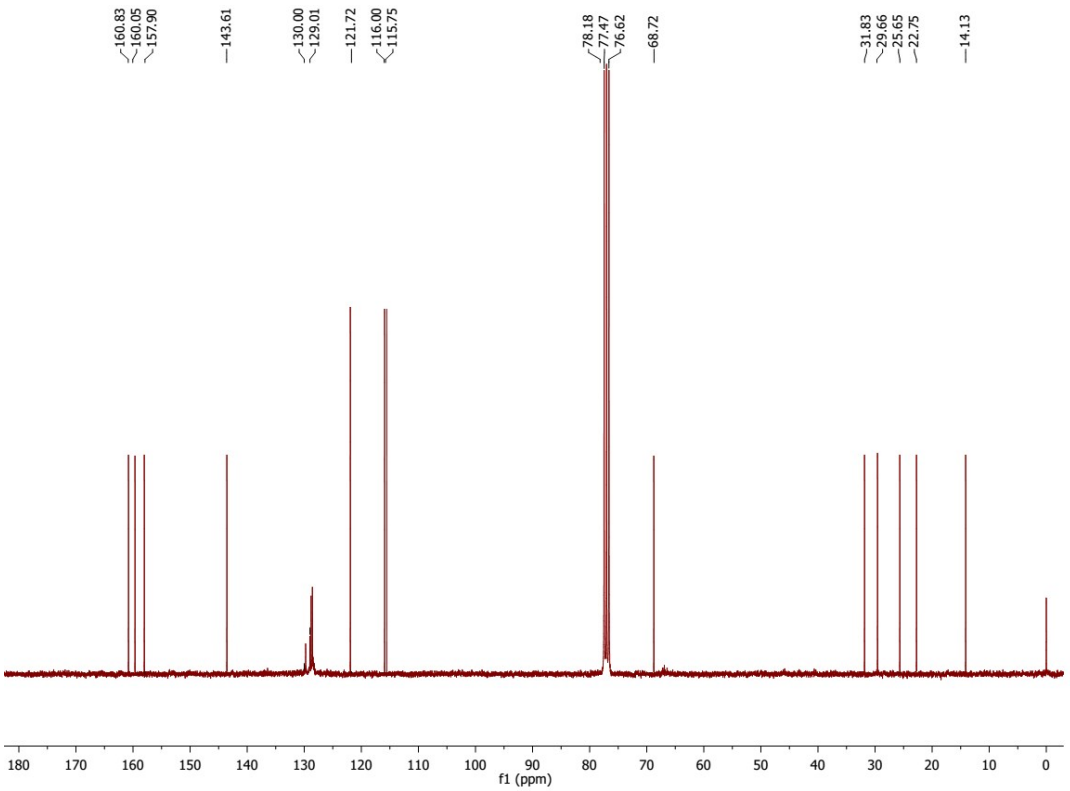

Figure S_7: ^{13}C NMR of compound $1C_6$.

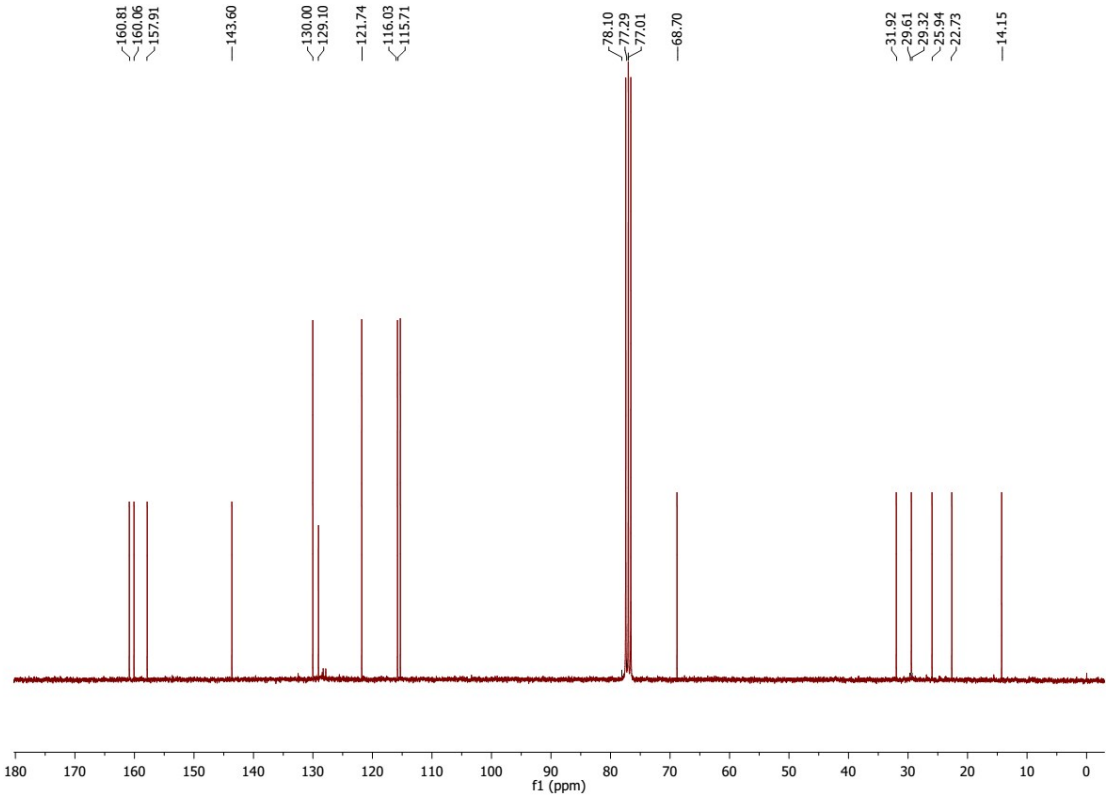

Figure S_8: ^{13}C NMR of compound $1C_8$.

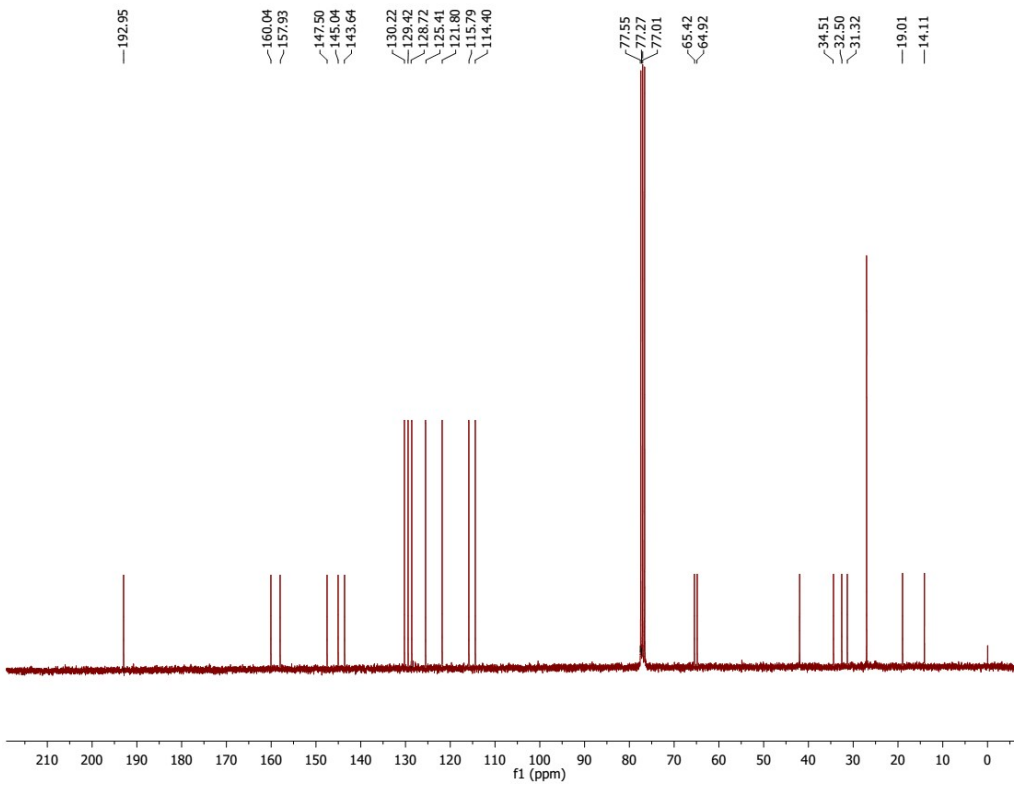

Figure S$_9$: ^{13}C NMR of compound 1f$_4$.

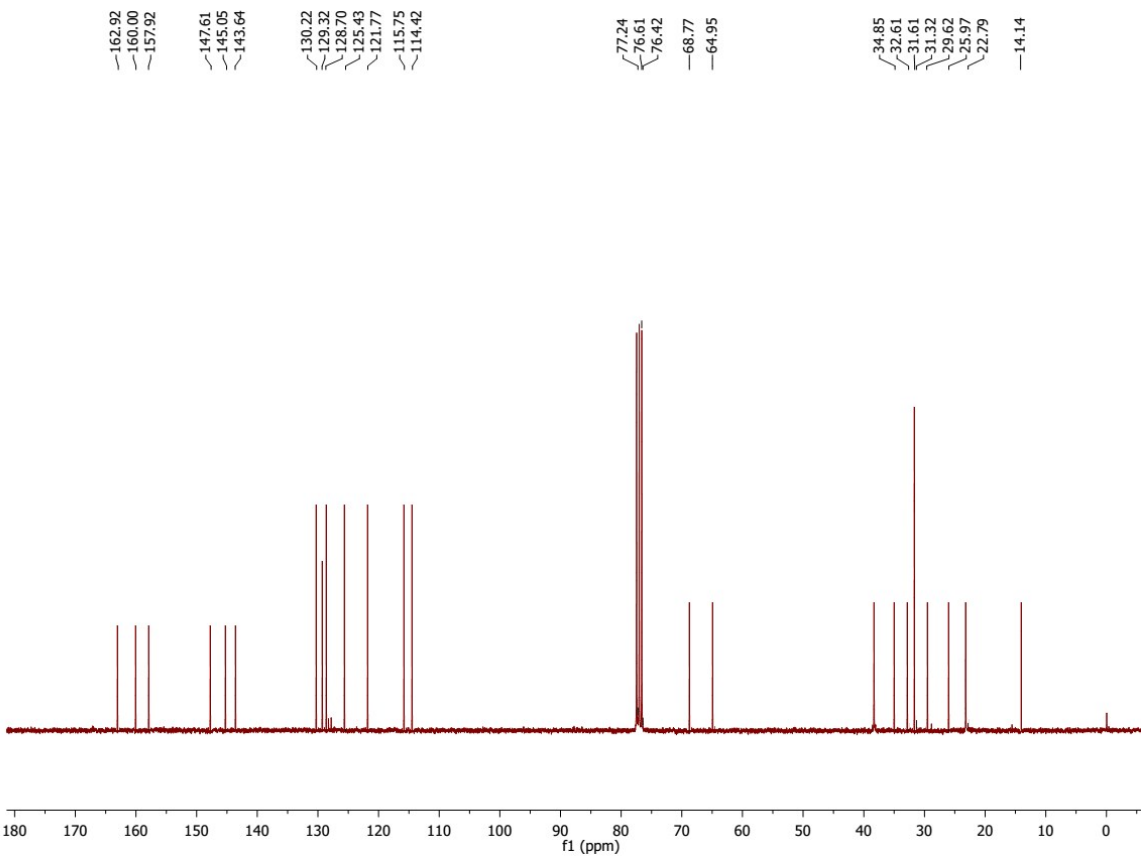

Figure S_{10}: ^{13}C NMR of compound $1f_6$.

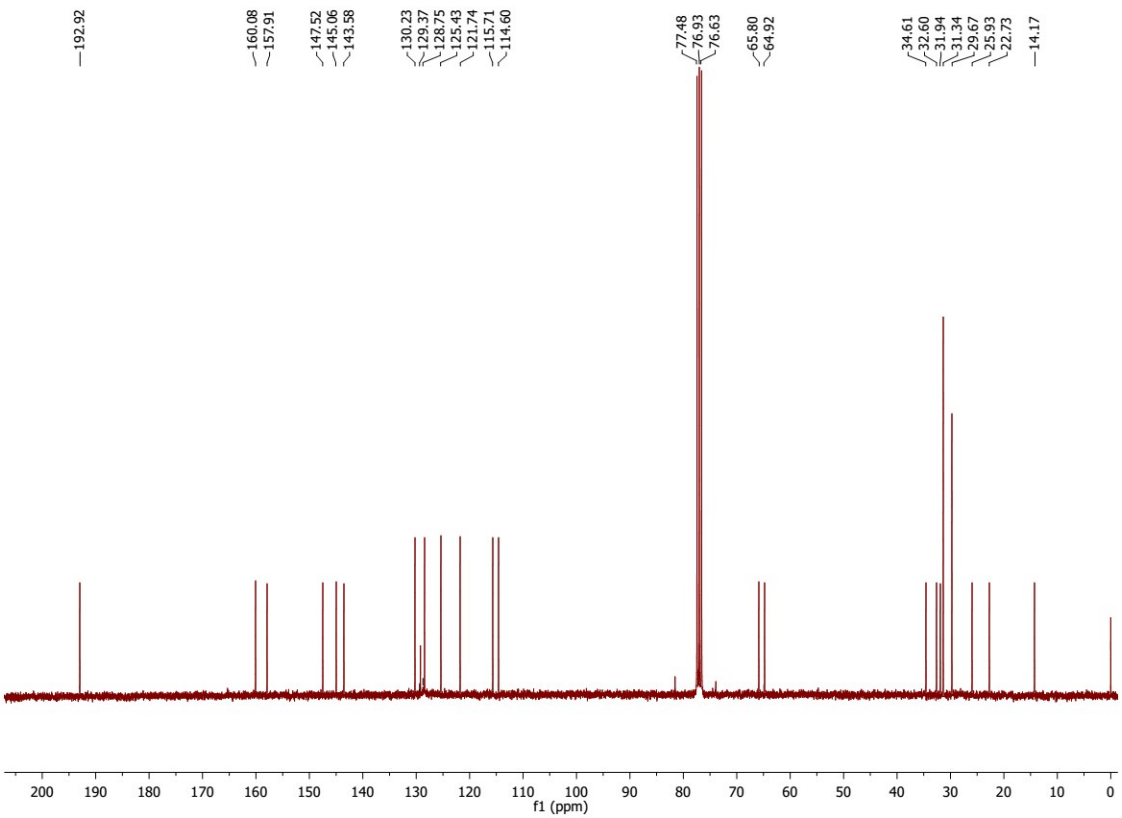

Figure S_{11}: ^{13}C NMR of compound $1f_8$.

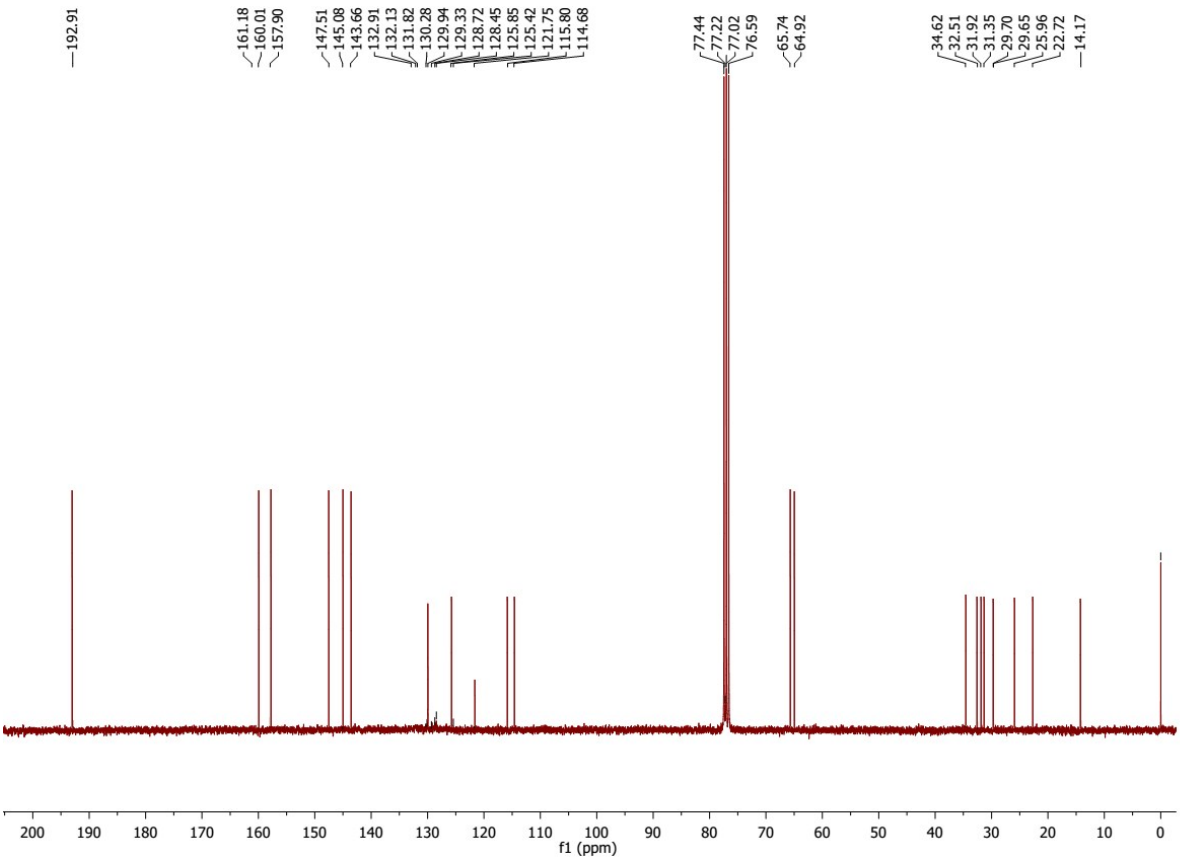

Figure S_{12}: ^{13}C NMR of compound $1f_{12}$.

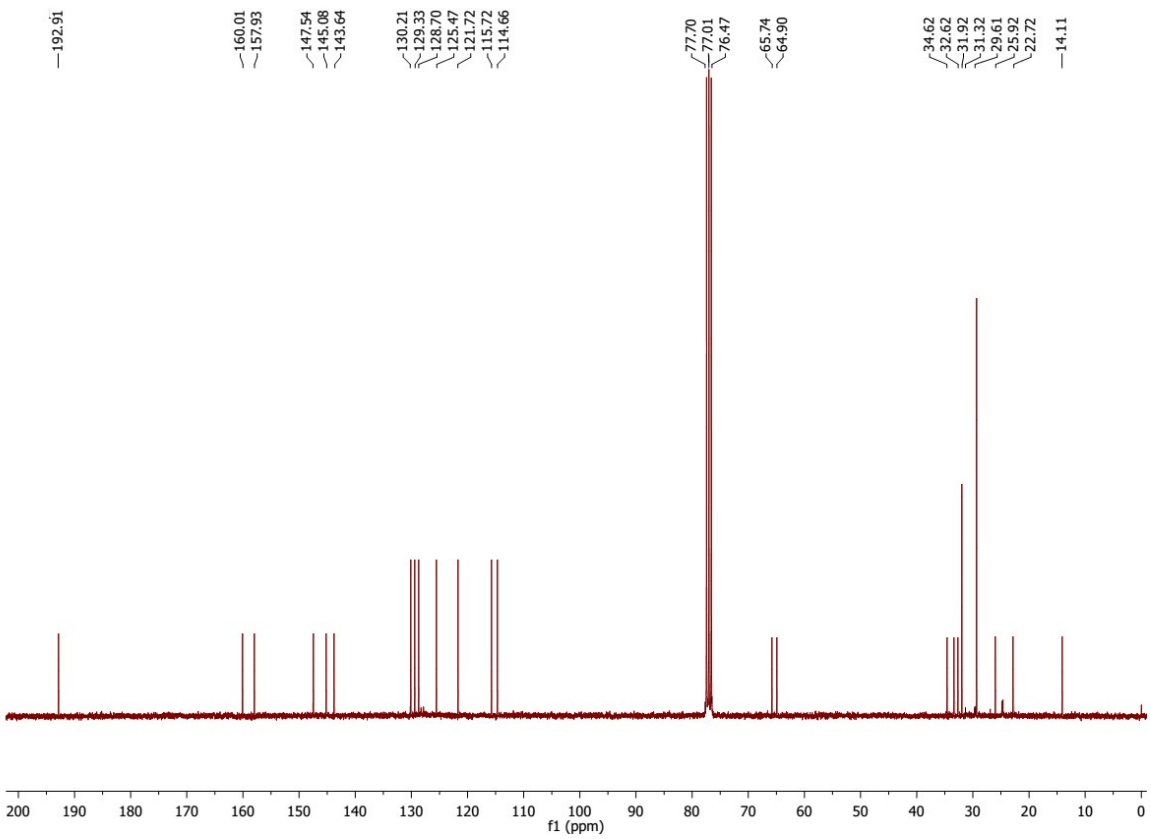

Figure S_{13}: ^{13}C NMR of compound $1f_{14}$.

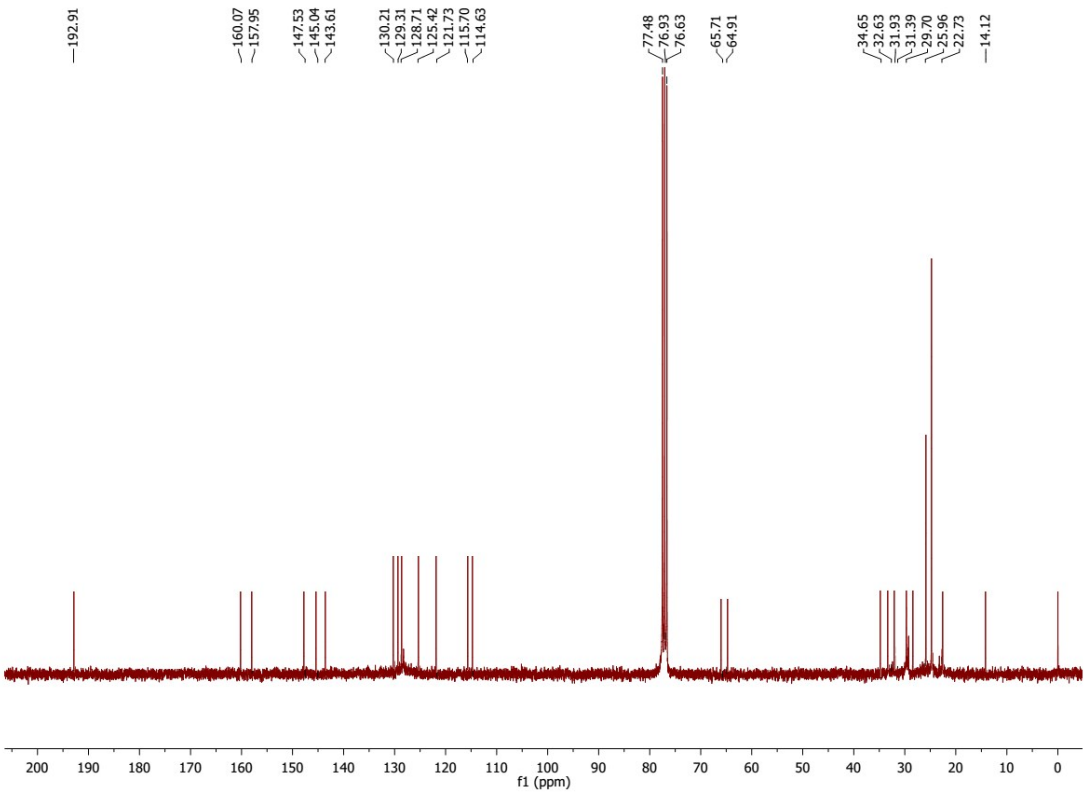

Figure S_{14}: ^{13}C NMR of compound $1f_{16}$.

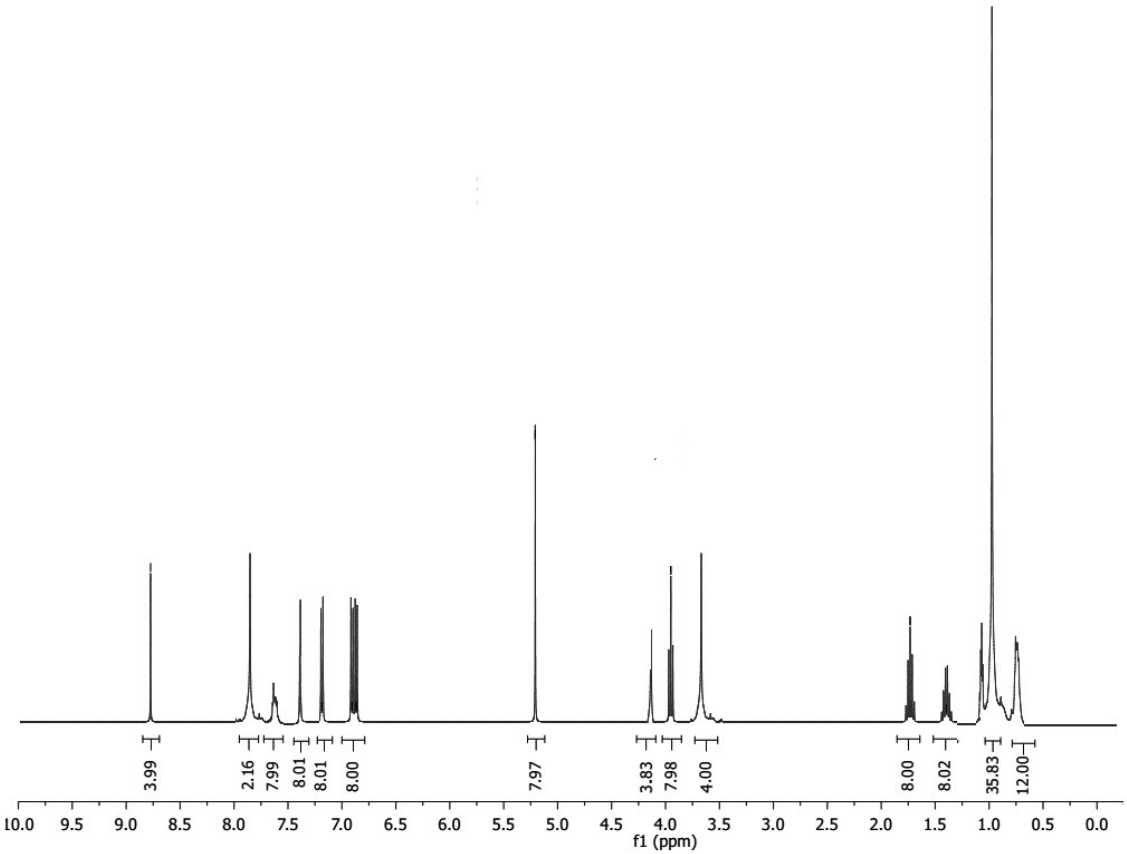

Figure S_{15}: ^{1}H NMR of compound $1f_4$.

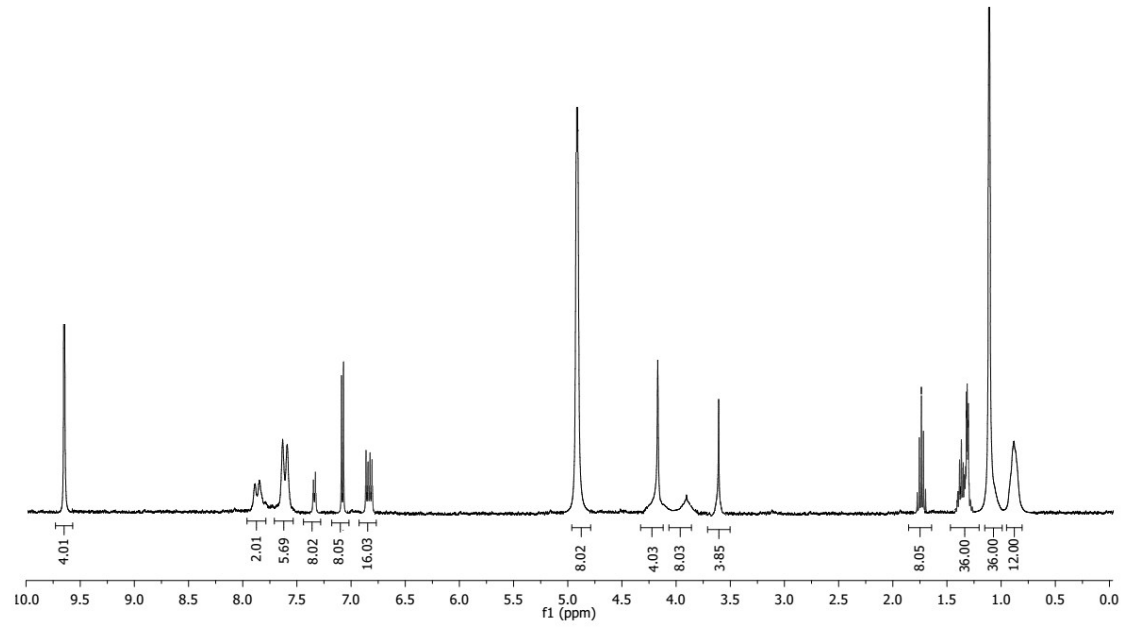

Figure S_{16}: ^{1}H NMR of compound $1f_6$.

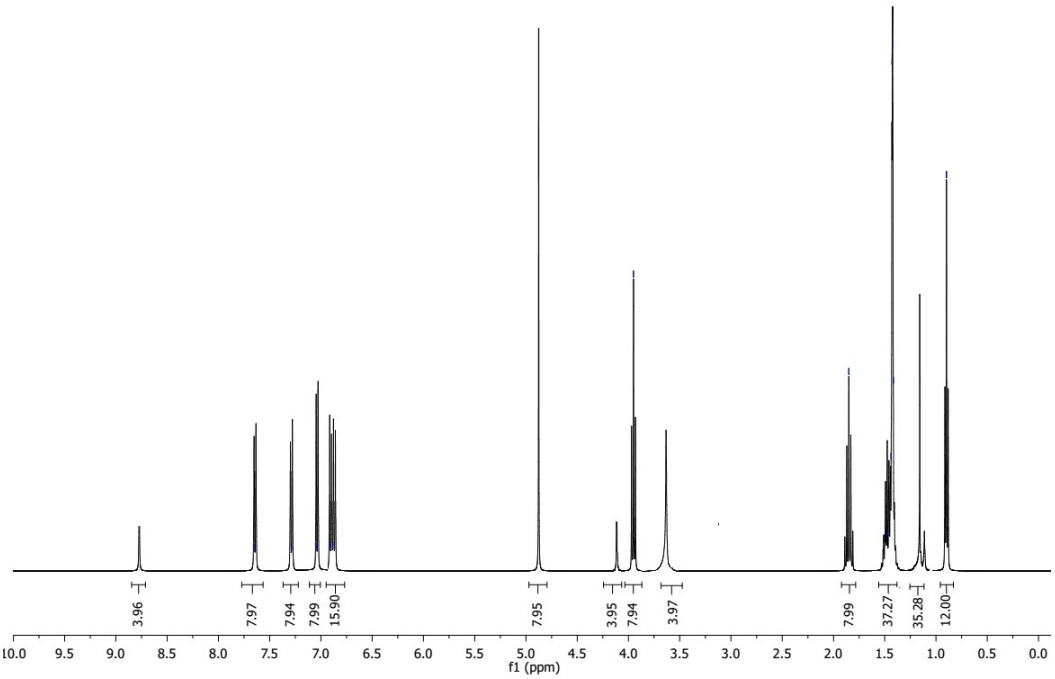

Figure S_{17}: ^{1}H NMR of compound $1f_8$.

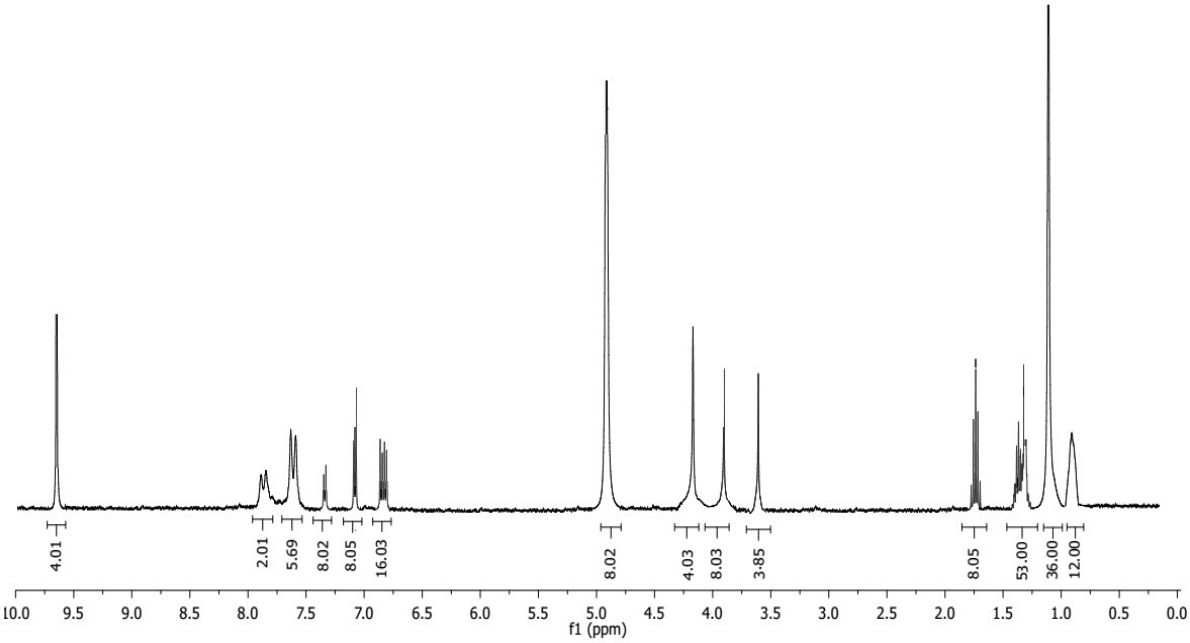

Figure S_{18}: ^{1}H NMR of compound $1f_{10}$.

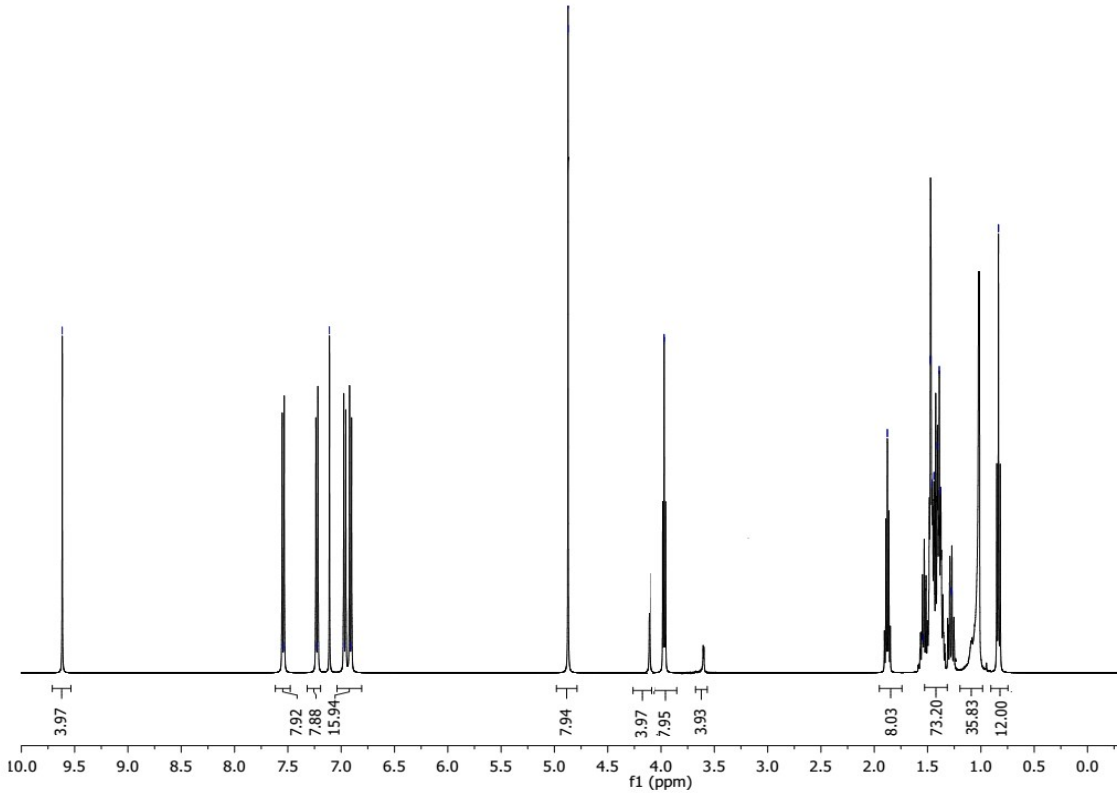

Figure S_{19}: ^{1}H NMR of compound $1f_{12}$.

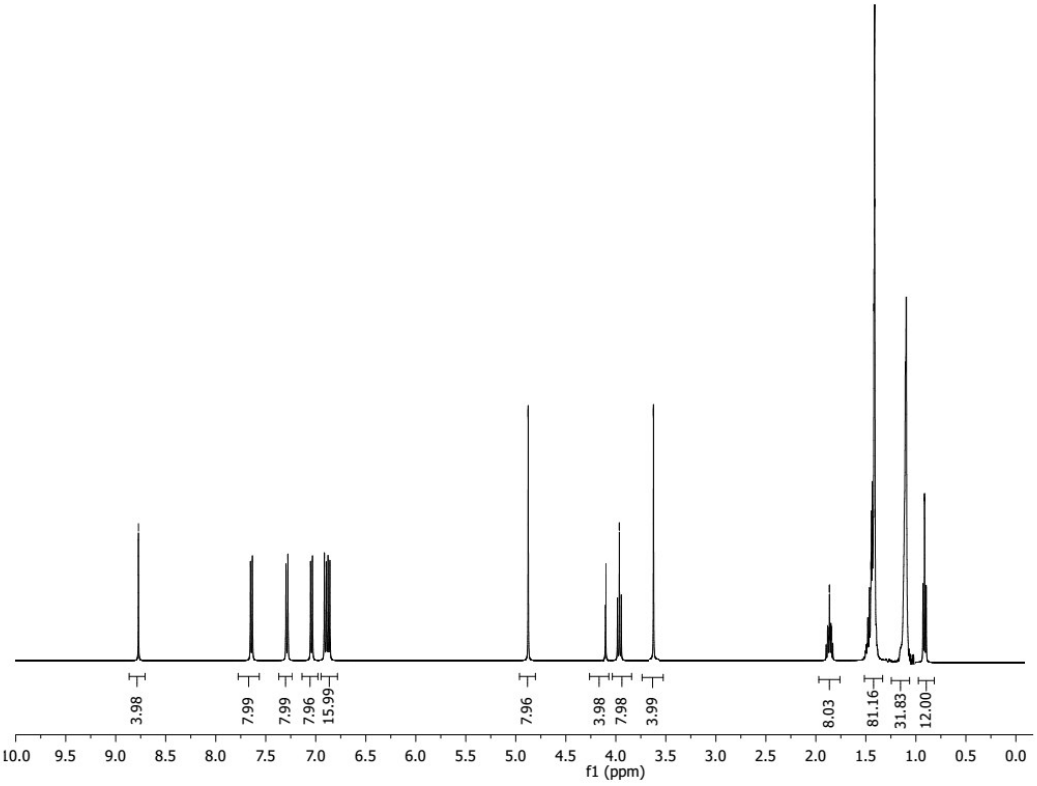

Figure S_{20}: ^{1}H NMR of compound $1f_{14}$.

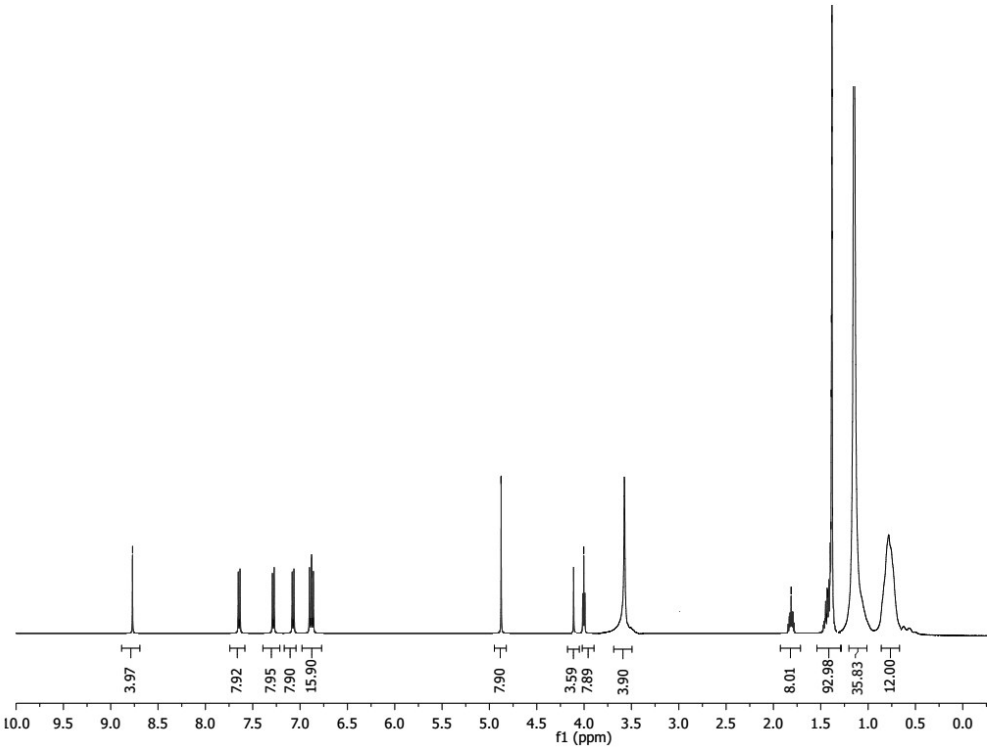

Figure S_{21}: ^{1}H NMR of compound $1f_{16}$.

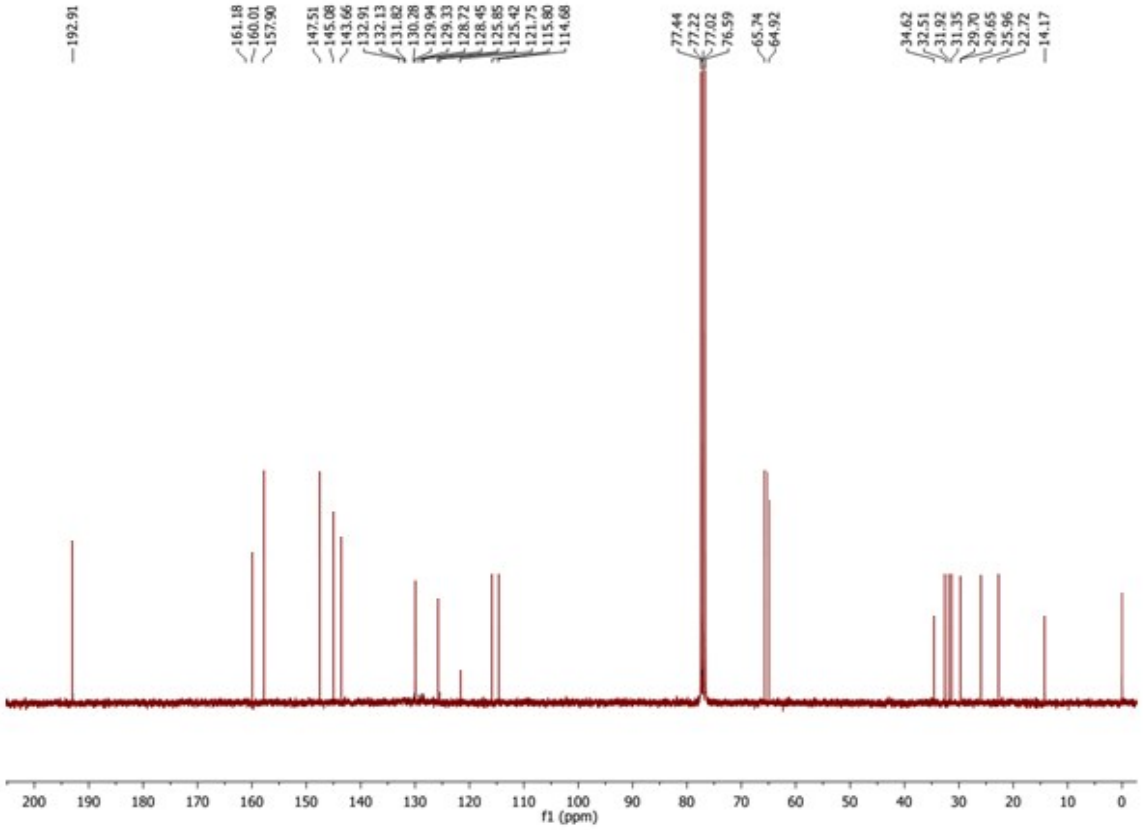

Figure S_{22}: ^{13}C NMR of compound $1f_{10}$.

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