

## Supplementary Material

### Solvent-free MeSO<sub>3</sub>H-promoted cyclotrimerization of acetophenones, effects of halogen and methoxy substituents on the reaction

Dumisile G. Matsala and Ishmael B. Masesane

*Department of Chemistry, University of Botswana, Private Bag 00704, Gaborone, Botswana*

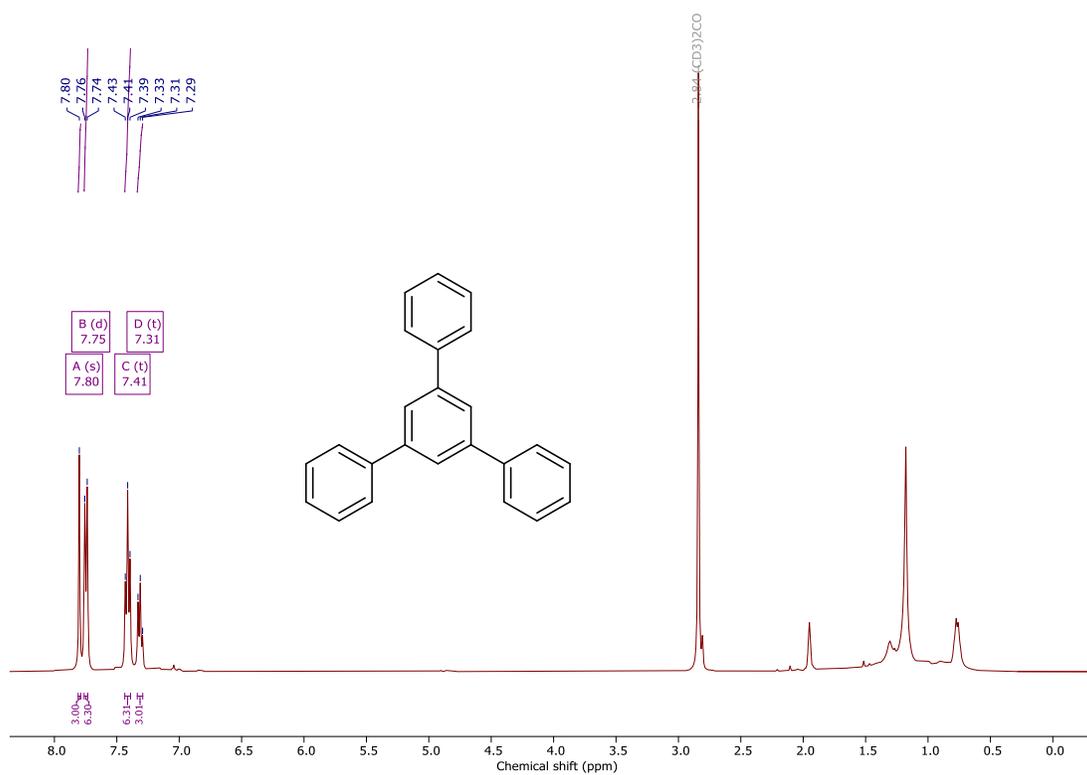
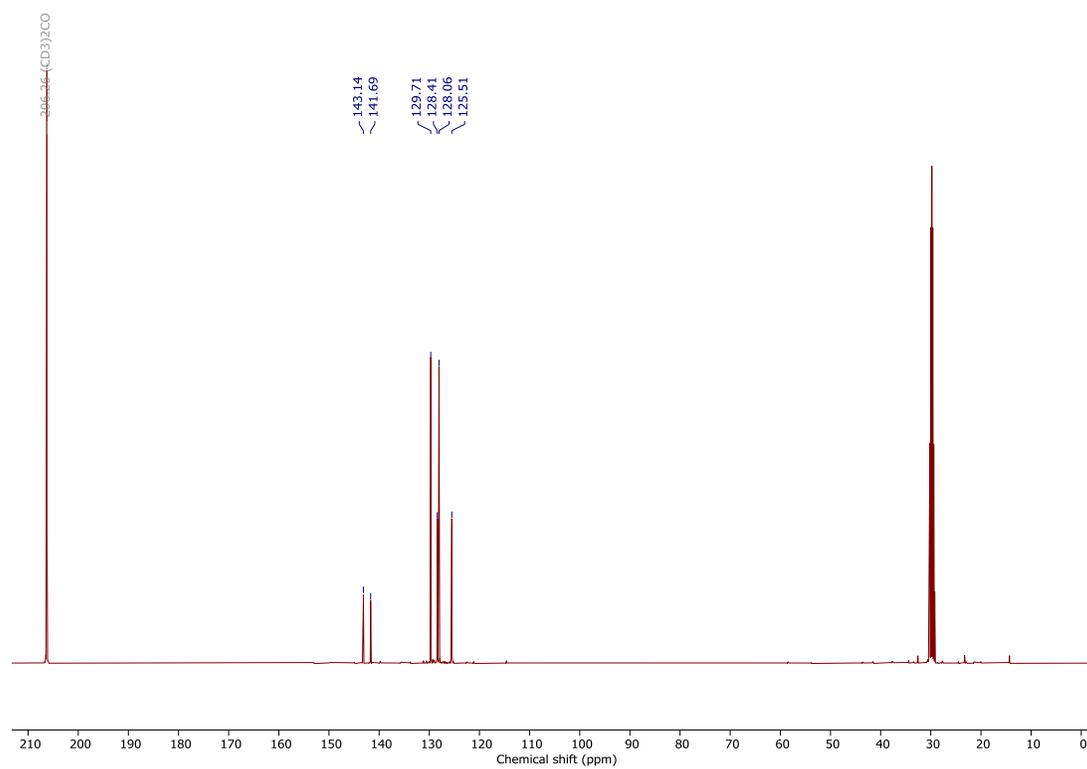
*Email: [masesane@ub.ac.bw](mailto:masesane@ub.ac.bw)*

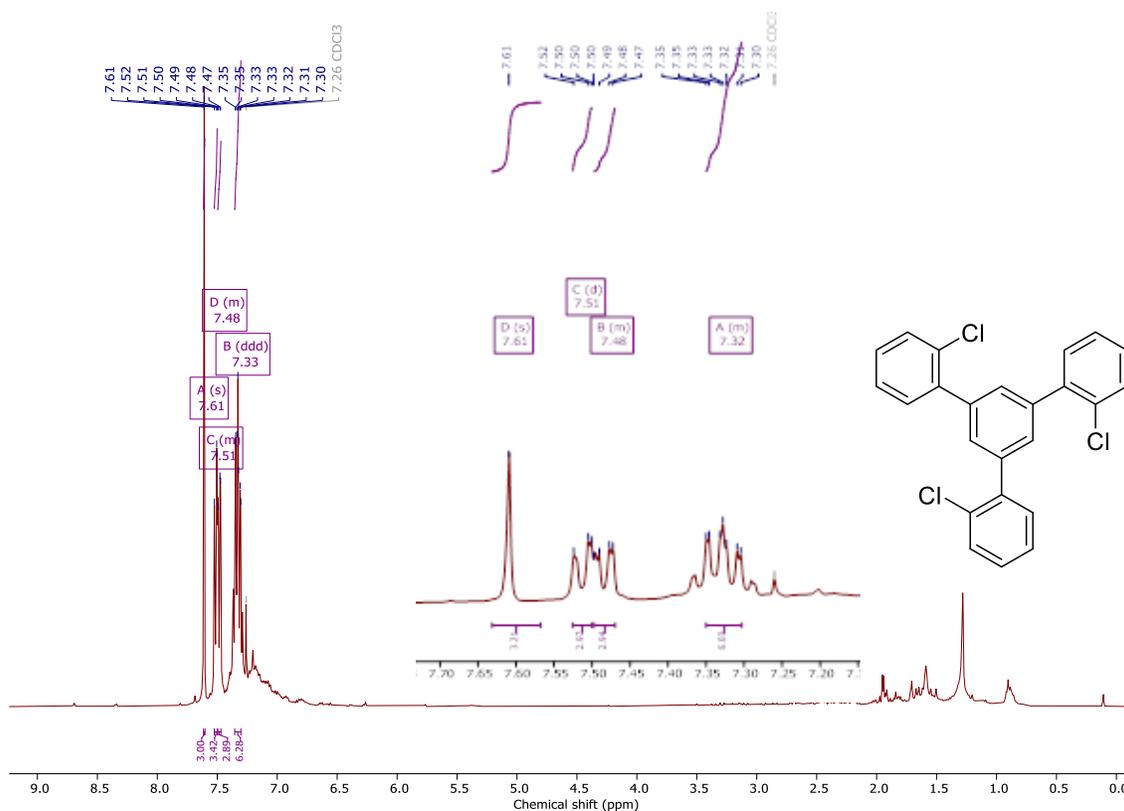
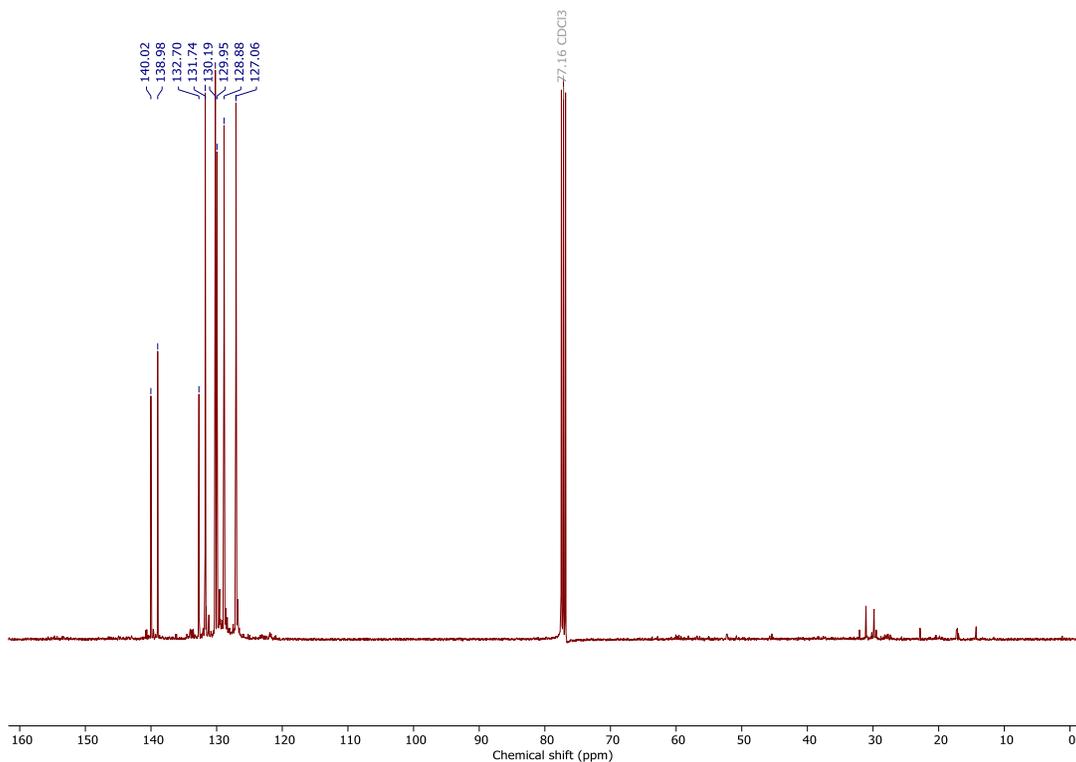
#### Table of Contents

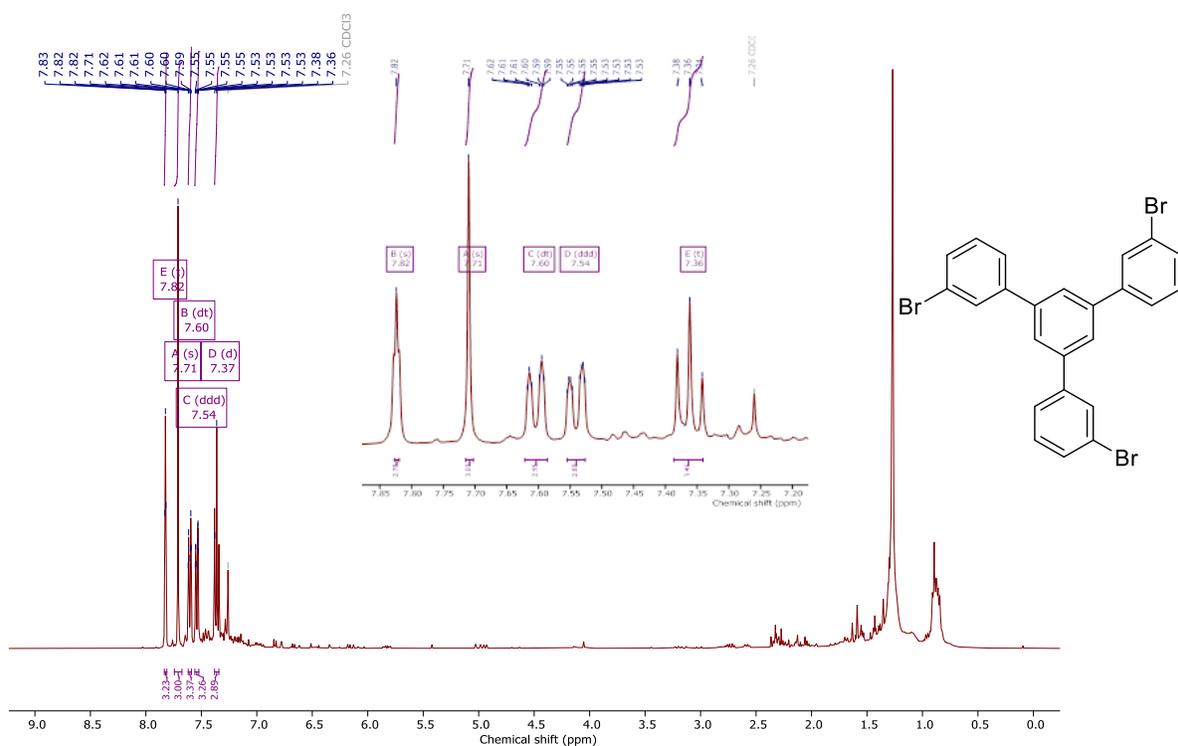
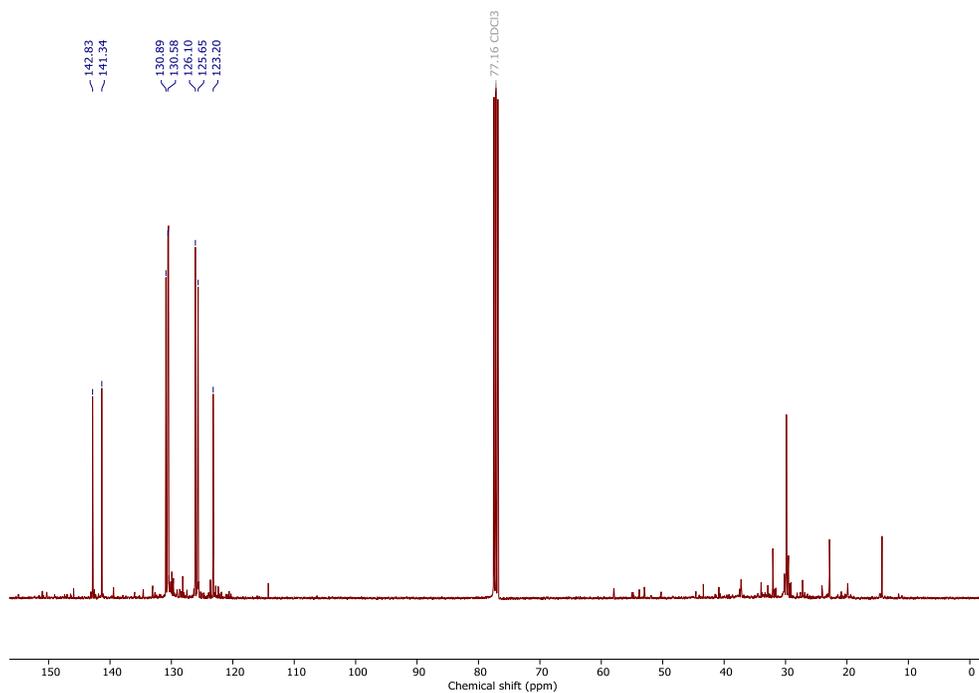
Typical procedure .....	S2
<sup>1</sup> H and <sup>13</sup> C of prepared compounds.....	S3
XRD crystal structure analysis data.....	S9

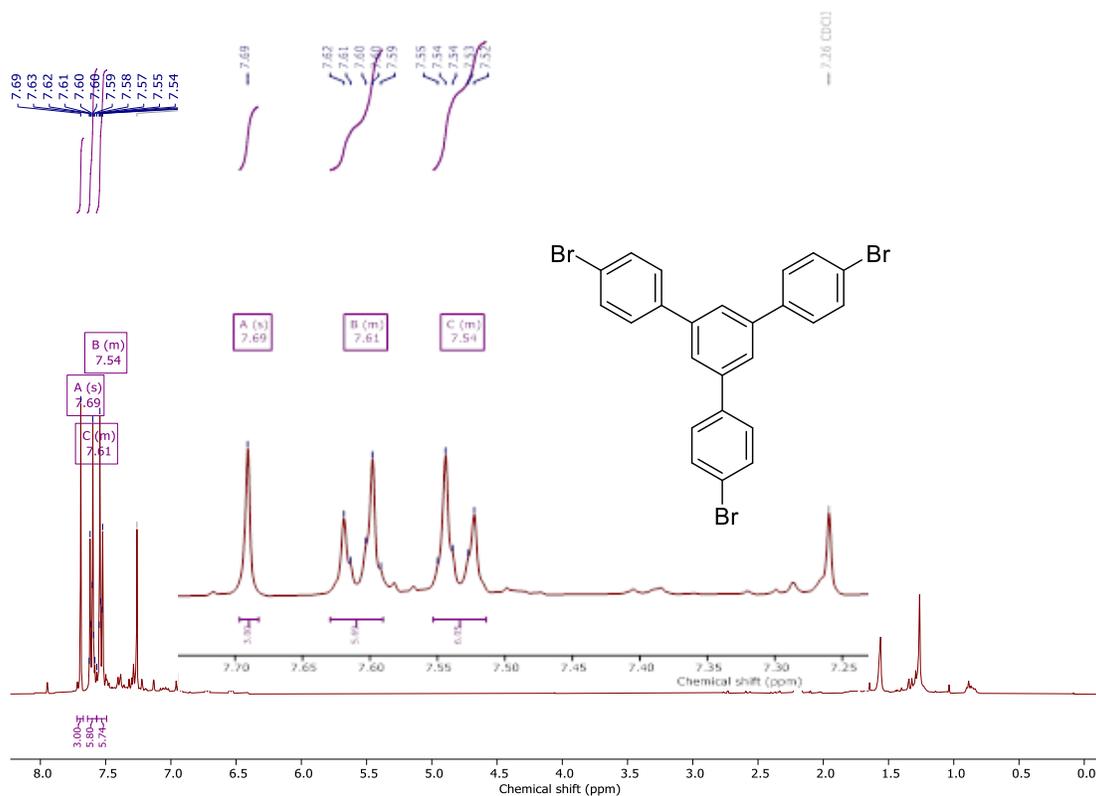
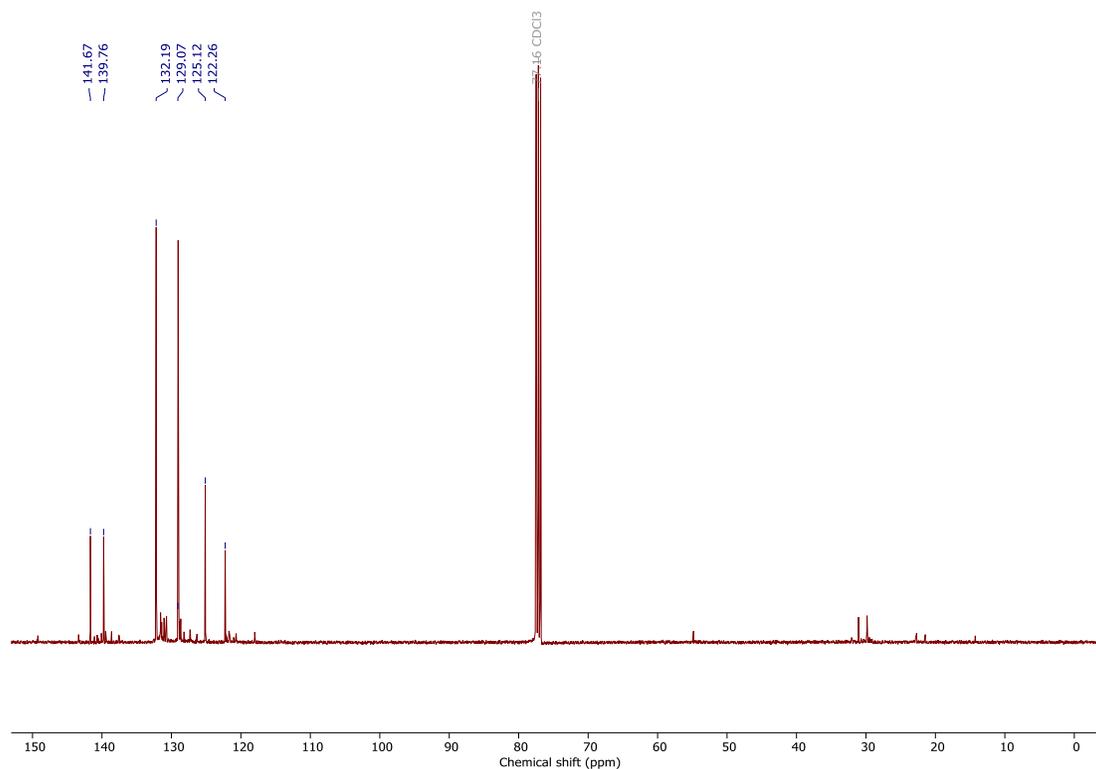
**Typical procedure**

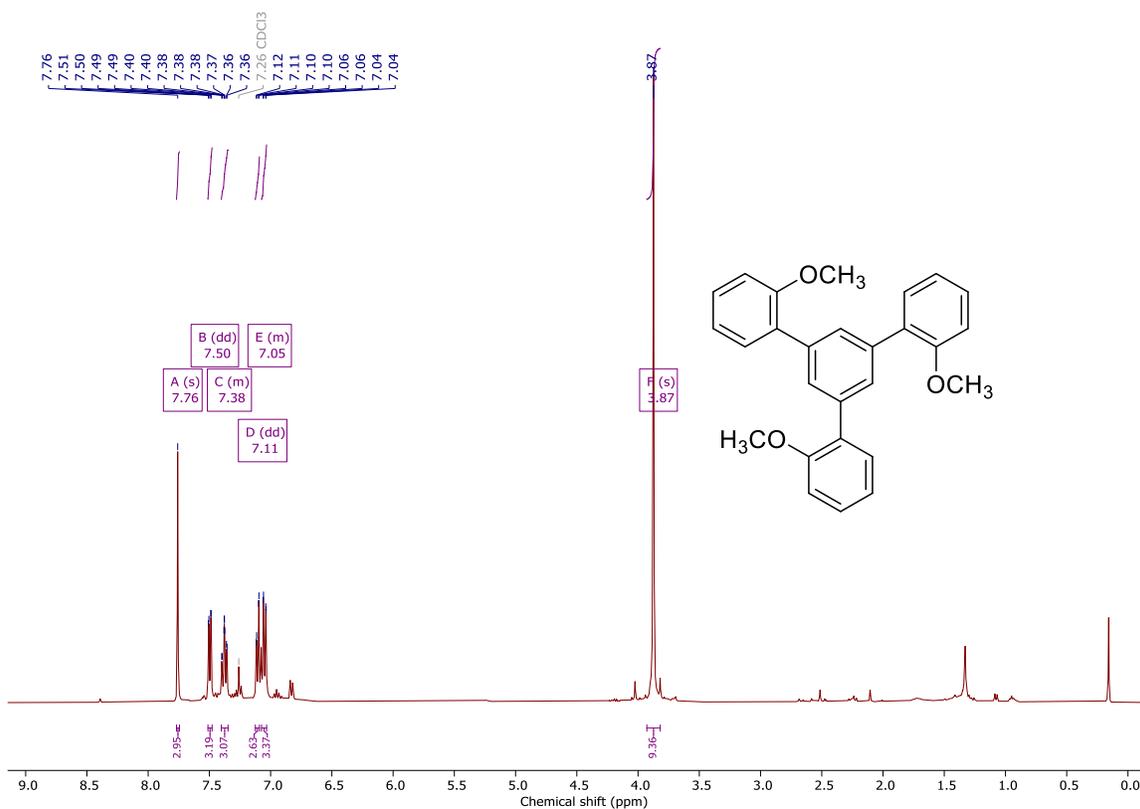
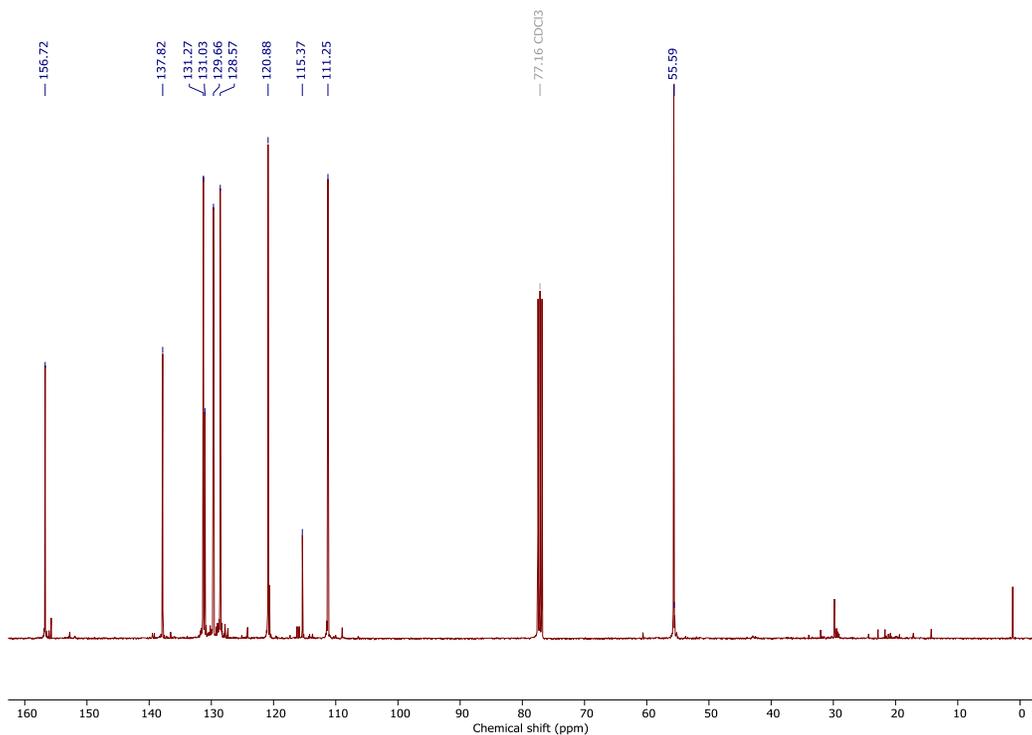
Acetophenone (1.47 g, 0.0122 mol) was treated with methanesulfonic acid (1.0 ml, 0.0122mol) and heated for at 65°C until acetophenone could not be detected by TLC (30 minutes). Thereafter, the reaction mixture was quenched with sodium hydrogen carbonate and extracted three times with chloroform. The organic layers were mixed, dried with MgSO<sub>4</sub> and concentrated under pressure. The crude product was purified using silica gel column chromatography and eluting with hexane.

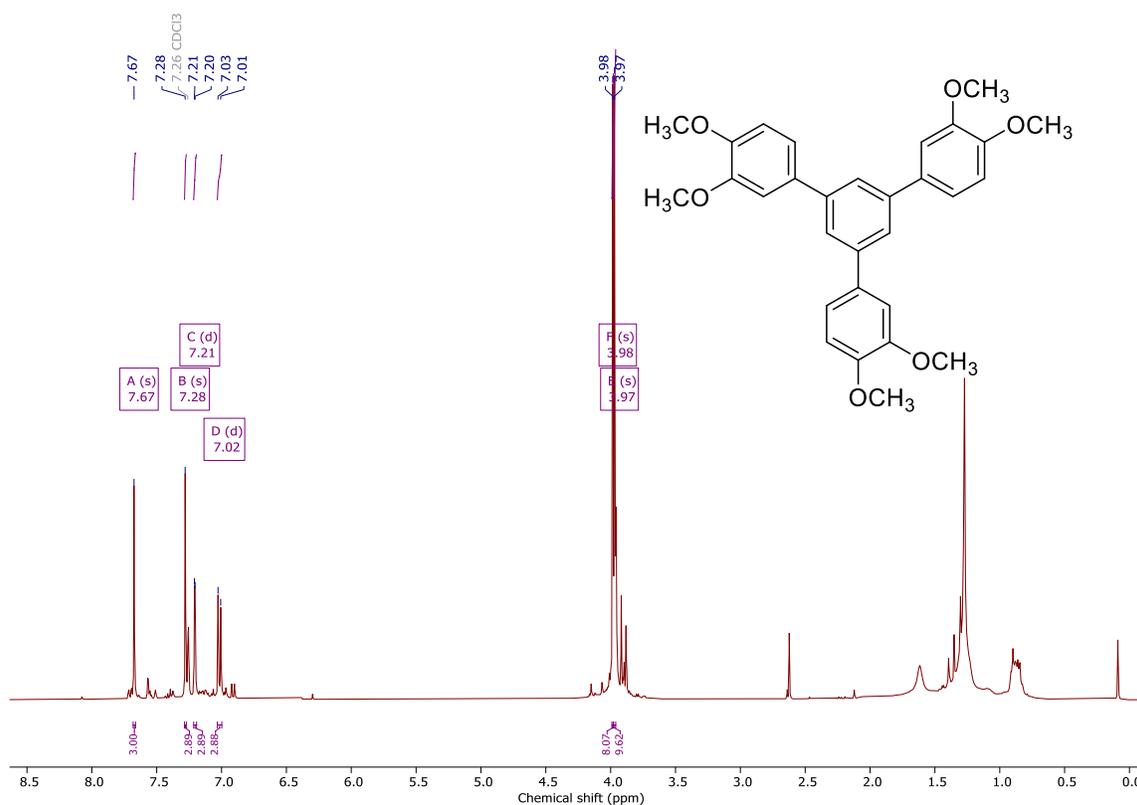
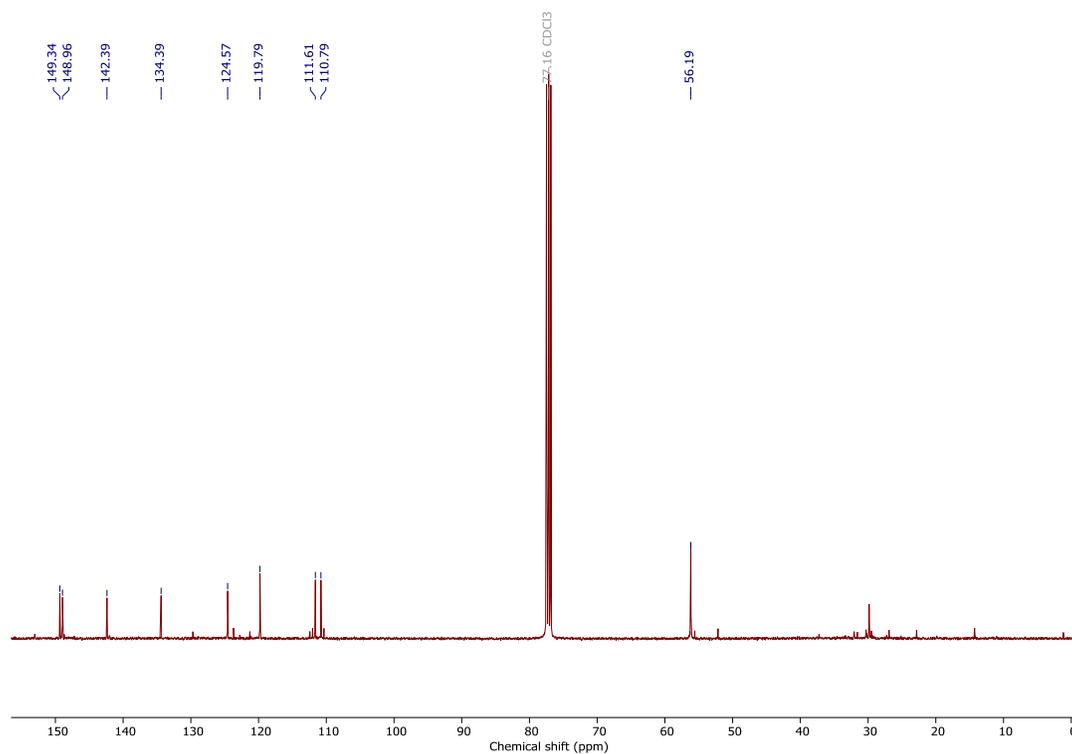
Appendix 1:  $^1\text{H}$  NMR spectrum of 1,3,5-triphenylbenzeneAppendix 2:  $^{13}\text{C}$  NMR spectrum of 1,3,5-triphenylbenzene

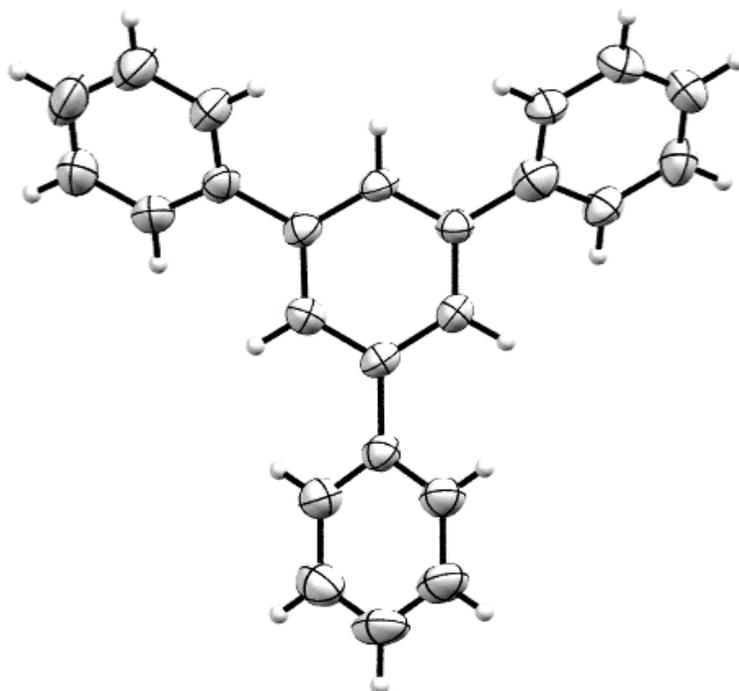
Appendix 3: <sup>1</sup>H NMR spectrum of 1,3,5-tris(2-chlorophenyl)benzeneAppendix 4: <sup>13</sup>C NMR spectrum of 1,3,5-tris(2-chlorophenyl)benzene

Appendix 5:  $^1\text{H}$  NMR spectrum of 1,3,5-tris(3-bromophenyl)benzeneAppendix 6:  $^{13}\text{C}$  NMR spectrum of 1,3,5-tris(3-bromophenyl)benzene

Appendix 7:  $^1\text{H}$  NMR spectrum of 1,3,5-tris(4-bromophenyl)benzeneAppendix 8:  $^{13}\text{C}$  NMR Spectrum of 1,3,5-tris(4-bromophenyl)benzene

Appendix 9:  $^1\text{H}$  NMR spectrum of 1,3,5-tris(2-methoxyphenyl)benzeneAppendix 10:  $^{13}\text{C}$  NMR spectrum of 1,3,5-tris(2-methoxyphenyl)benzene

Appendix 11:  $^1\text{H}$  NMR spectrum of 1,3,5-tris(3,4-dimethoxyphenyl)benzeneAppendix 12:  $^{13}\text{C}$  NMR spectrum of 1,3,5-tris(3,4-dimethoxyphenyl)benzene

**Appendix 13:** Single crystal XRD structure and data of 1,3,5-triphenylbenzene

**Table 1.** Crystal data and structure refinement for DW22\_0ma.

Identification code	DW22_0ma
Empirical formula	C <sub>24</sub> H <sub>18</sub>
Formula weight	306.38
Temperature/K	294.0
Crystal system	orthorhombic
Space group	Pna2 <sub>1</sub>
a/Å	7.6003(10)
b/Å	19.750(2)
c/Å	11.2507(12)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	1688.8(4)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.205
μ/mm <sup>-1</sup>	0.068
F(000)	648.0
Crystal size/mm <sup>3</sup>	0.85 × 0.36 × 0.14
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	6.764 to 48.87
Index ranges	-8 ≤ h ≤ 8, -22 ≤ k ≤ 22, -13 ≤ l ≤ 13
Reflections collected	26546
Independent reflections	2767 [R <sub>int</sub> = 0.1685, R <sub>sigma</sub> = 0.0559]
Data/restraints/parameters	2767/1/217
Goodness-of-fit on F <sup>2</sup>	1.018
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0431, wR <sub>2</sub> = 0.0726
Final R indexes [all data]	R <sub>1</sub> = 0.0742, wR <sub>2</sub> = 0.0810
Largest diff. peak/hole / e Å <sup>-3</sup>	0.12/-0.17
Flack parameter	0.1(10)

**Table 2.** Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for DW22\_0ma.  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalised  $U_{ij}$  tensor.

Atom	x	y	z	U(eq)
C24	2189(4)	3911.2(16)	6544(3)	39.1(9)
C23	3173(4)	3306.7(15)	3412(3)	38.1(8)
C1	1100(5)	5750(2)	8391(4)	68.6(11)
C2	2028(5)	5246(2)	8933(4)	64.1(11)
C3	2401(4)	4652.4(18)	8338(3)	54.4(9)
C4	1832(4)	4555.3(15)	7176(3)	41.7(8)
C5	2193(4)	3299.2(16)	7145(3)	43.2(8)
C6	2493(4)	2685.5(17)	6570(3)	39.7(8)
C7	2476(4)	2038.8(16)	7238(3)	42.1(8)
C8	1824(5)	1452.2(17)	6738(3)	52.8(9)
C9	1817(5)	850.3(18)	7361(3)	65.8(11)
C10	2461(5)	826(2)	8487(4)	73.8(12)
C11	3867(5)	3325.0(19)	981(3)	61.9(11)
C12	2841(5)	2824.4(19)	1465(3)	61.3(11)
C13	2501(5)	2812.5(17)	2665(3)	48.5(10)
C14	2811(4)	3300.3(16)	4711(3)	37.2(8)
C15	2801(4)	2698.8(17)	5349(3)	41.1(9)
C16	532(5)	5669.3(17)	7239(4)	64.6(10)
C17	905(4)	5077.9(16)	6642(3)	51.9(9)
C18	2507(4)	3899.0(16)	5323(3)	41.7(8)
C19	3130(6)	1401(2)	9007(4)	70.9(11)
C20	3127(5)	2002.9(18)	8383(3)	58.4(10)
C21	4188(5)	3811.6(16)	2906(3)	49.2(9)
C22	4544(5)	3820.7(18)	1704(3)	61.3(11)

**Table 3.** Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for DW22\_0ma. The Anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^*^2U_{11}+2hka^*b^*U_{12}+\dots]$ .

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
C24	43(2)	31(2)	43(2)	1.0(16)	0.1(16)	0.0(14)
C23	40.3(18)	30.8(19)	43.3(19)	0.6(17)	-0.6(17)	4.0(16)
C1	71(3)	45(3)	89(3)	-21(2)	33(3)	-5(2)
C2	69(3)	64(3)	59(2)	-16(2)	17(2)	-14(2)
C3	63(2)	42(2)	58(3)	-2.0(19)	7(2)	-0.2(17)
C4	45(2)	34(2)	46(2)	-0.8(16)	6.9(19)	-3.0(16)
C5	47(2)	42(2)	40.9(18)	-2.1(17)	5.0(17)	2.2(15)
C6	40.5(19)	34(2)	45(2)	2.1(16)	2.4(16)	-1.2(16)
C7	43(2)	36(2)	47(2)	3.5(17)	7.1(19)	6.1(16)
C8	58(2)	39(2)	61(2)	6.9(19)	0.2(19)	1.0(18)
C9	76(3)	39(2)	83(3)	8(2)	7(2)	-2.4(18)
C10	95(3)	52(3)	74(3)	26(2)	20(3)	15(2)
C11	86(3)	59(3)	41(2)	-2(2)	9(2)	6(2)
C12	76(3)	58(3)	50(2)	-14(2)	0(2)	-6(2)
C13	59(3)	39(2)	47(2)	-2.1(16)	3.0(17)	-9.7(18)
C14	39.2(19)	29(2)	43(2)	-2.5(16)	-2.1(16)	0.4(15)
C15	46(2)	29(2)	48(2)	-5.4(16)	-2.1(16)	0.3(16)
C16	64(3)	45(2)	85(3)	-5(2)	20(2)	9.2(18)
C17	57(2)	41(2)	57(2)	-4.4(19)	9.4(18)	5.6(18)
C18	46(2)	33(2)	46(2)	5.5(15)	-0.9(15)	0.1(17)
C19	100(3)	63(3)	50(2)	11(2)	7(2)	20(3)
C20	86(3)	43(2)	47(2)	-1(2)	6(2)	11.2(19)
C21	57(2)	39(2)	51(2)	-3.4(16)	2.8(17)	-5.6(18)
C22	72(3)	52(3)	60(3)	9(2)	15(2)	-7(2)

**Table 4.** Bond Lengths for DW22\_0ma.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C24	C4	1.482(4)	C7	C8	1.380(4)
C24	C5	1.385(4)	C7	C20	1.381(4)
C24	C18	1.395(4)	C8	C9	1.380(4)
C23	C13	1.386(4)	C9	C10	1.359(5)
C23	C14	1.487(4)	C10	C19	1.375(5)
C23	C21	1.383(4)	C11	C12	1.372(5)
C1	C2	1.363(5)	C11	C22	1.373(5)
C1	C16	1.376(5)	C12	C13	1.375(4)
C2	C3	1.380(5)	C14	C15	1.388(4)
C3	C4	1.390(4)	C14	C18	1.388(4)
C4	C17	1.386(4)	C16	C17	1.377(4)
C5	C6	1.393(4)	C19	C20	1.380(5)
C6	C7	1.482(4)	C21	C22	1.379(4)
C6	C15	1.394(4)			

**Table 5.** Bond Angles for DW22\_0ma.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	C24	C4	121.0(3)	C20	C7	C6	120.9(3)
C5	C24	C18	117.7(3)	C7	C8	C9	121.1(3)
C18	C24	C4	121.3(3)	C10	C9	C8	120.2(4)
C13	C23	C14	121.5(3)	C9	C10	C19	120.0(4)
C21	C23	C13	117.6(3)	C12	C11	C22	119.5(3)
C21	C23	C14	120.9(3)	C11	C12	C13	120.6(3)
C2	C1	C16	120.0(4)	C12	C13	C23	121.0(3)
C1	C2	C3	120.6(4)	C15	C14	C23	121.1(3)
C2	C3	C4	120.6(3)	C18	C14	C23	120.7(3)
C3	C4	C24	120.8(3)	C18	C14	C15	118.2(3)
C17	C4	C24	121.6(3)	C14	C15	C6	121.8(3)
C17	C4	C3	117.6(3)	C1	C16	C17	119.5(4)
C24	C5	C6	122.2(3)	C16	C17	C4	121.7(4)
C5	C6	C7	120.8(3)	C14	C18	C24	122.1(3)
C5	C6	C15	118.0(3)	C10	C19	C20	119.6(4)
C15	C6	C7	121.2(3)	C19	C20	C7	121.3(4)
C8	C7	C6	121.3(3)	C22	C21	C23	121.5(3)
C8	C7	C20	117.8(3)	C11	C22	C21	119.9(4)

**Table 6** .Torsion Angles for DW22\_0ma.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C24	C4	C17	C16	178.2(3)	C8	C7	C20	C19	0.1(5)
C24	C5	C6	C7	-179.6(3)	C8	C9	C10	C19	-0.2(6)
C24	C5	C6	C15	0.1(5)	C9	C10	C19	C20	0.6(6)
C23	C14	C15	C6	178.9(3)	C10	C19	C20	C7	-0.5(6)
C23	C14	C18	C24	-179.1(3)	C11	C12	C13	C23	0.5(6)
C23	C21	C22	C11	0.8(6)	C12	C11	C22	C21	0.0(6)
C1	C2	C3	C4	-0.2(5)	C13	C23	C14	C15	39.8(4)
C1	C16	C17	C4	0.4(5)	C13	C23	C14	C18	-141.4(3)
C2	C1	C16	C17	0.2(5)	C13	C23	C21	C22	-0.9(5)
C2	C3	C4	C24	-178.4(3)	C14	C23	C13	C12	179.8(3)
C2	C3	C4	C17	0.8(5)	C14	C23	C21	C22	179.5(3)
C3	C4	C17	C16	-0.9(5)	C15	C6	C7	C8	-35.5(5)
C4	C24	C5	C6	178.9(3)	C15	C6	C7	C20	144.0(3)
C4	C24	C18	C14	-178.8(3)	C15	C14	C18	C24	-0.3(5)
C5	C24	C4	C3	34.9(5)	C16	C1	C2	C3	-0.3(5)
C5	C24	C4	C17	-144.2(3)	C18	C24	C4	C3	-146.0(3)
C5	C24	C18	C14	0.4(5)	C18	C24	C4	C17	34.9(5)
C5	C6	C7	C8	144.2(3)	C18	C24	C5	C6	-0.3(5)
C5	C6	C7	C20	-36.3(4)	C18	C14	C15	C6	0.1(5)
C5	C6	C15	C14	0.0(5)	C20	C7	C8	C9	0.2(5)
C6	C7	C8	C9	179.7(3)	C21	C23	C13	C12	0.3(5)
C6	C7	C20	C19	-179.4(3)	C21	C23	C14	C15	-140.6(3)
C7	C6	C15	C14	179.7(3)	C21	C23	C14	C18	38.1(4)
C7	C8	C9	C10	-0.2(6)	C22	C11	C12	C13	-0.6(6)

**Table 7.** Hydrogen Atom Coordinates ( $\text{\AA}\times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2\times 10^3$ ) for DW22\_0ma.

Atom	x	y	z	U(eq)
H1	849.72	6147.39	8800.73	82
H2	2413.68	5303.58	9711.35	77
H3	3039.8	4313.9	8717.59	65
H5	1987.67	3297.99	7960.01	52
H8	1382.48	1462.66	5967.25	63
H9	1369.17	460.46	7009.87	79
H10	2450.48	419.96	8906.38	89
H11	4102.77	3328.45	170.04	74
H12	2370.77	2490.27	976.84	74
H13	1810.62	2467.72	2979.98	58
H15	3004.19	2293.74	4950.26	49
H16	-98.3	6012.14	6865.09	78
H17	525.62	5027.55	5861.28	62
H18	2516.18	4305.38	4905.48	50
H19	3580.7	1385.22	9774.95	85
H20	3571.81	2391.61	8739.57	70
H21	4640.03	4152.71	3386.6	59
H22	5241.3	4161.98	1383.78	74

## Experimental

Single crystals of C<sub>24</sub>H<sub>18</sub> [DW22\_0ma] were [ ]. A suitable crystal was selected and [MiteGen Micromashes loops used to mount crystal] on a Bruker APEX-II CCD diffractometer. The crystal was kept at 294.0 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
2. Sheldrick, G.M. (2015). *Acta Cryst.* A71, 3-8.
3. Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

## Crystal structure determination of [DW22\_0ma]

**Crystal Data** for C<sub>24</sub>H<sub>18</sub> (*M* = 306.38 g/mol): orthorhombic, space group Pna2<sub>1</sub> (no. 33), *a* = 7.6003(10) Å, *b* = 19.750(2) Å, *c* = 11.2507(12) Å, *V* = 1688.8(4) Å<sup>3</sup>, *Z* = 4, *T* = 294.0 K,  $\mu(\text{MoK}\alpha) = 0.068 \text{ mm}^{-1}$ , *D*<sub>calc</sub> = 1.205 g/cm<sup>3</sup>, 26546 reflections measured (6.764° ≤ 2θ ≤ 48.87°), 2767 unique (*R*<sub>int</sub> = 0.1685, *R*<sub>sigma</sub> = 0.0559) which were used in all calculations. The final *R*<sub>1</sub> was 0.0431 (*I* > 2σ(*I*)) and *wR*<sub>2</sub> was 0.0810 (all data).

## Refinement model description

Number of restraints - 1, number of constraints - unknown.

## Details:

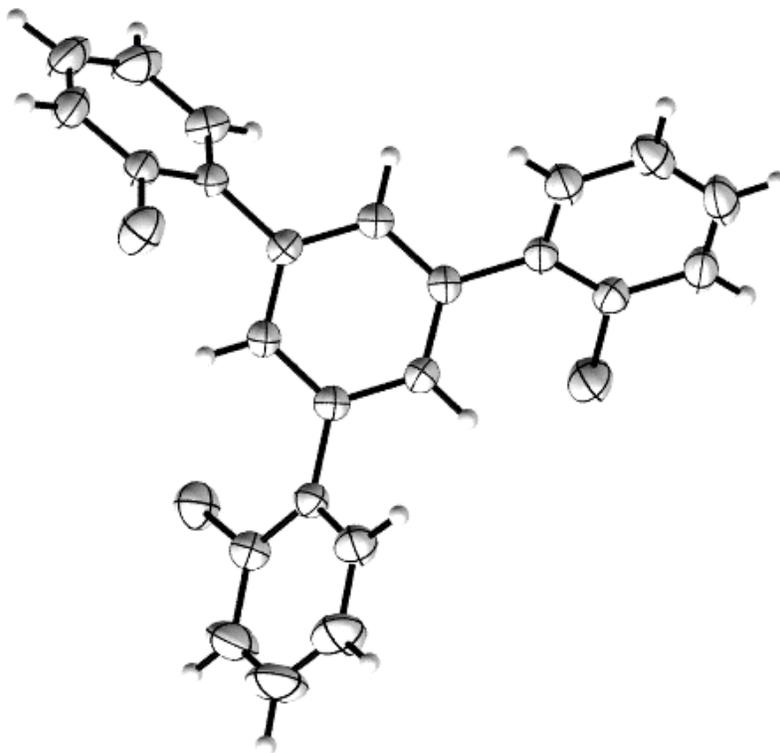
## 1. Fixed Uiso

At 1.2 times of:

All C(H) groups

## 2.a Aromatic/amide H refined with riding coordinates:

C1(H1), C2(H2), C3(H3), C5(H5), C8(H8), C9(H9), C10(H10), C11(H11), C12(H12),  
C13(H13), C15(H15), C16(H16), C17(H17), C18(H18), C19(H19), C20(H20), C21(H21),  
C22(H22)

**Appendix 14:** Single crystal XRD structure and data of 1,3,5-tris(2-chlorophenyl)benzene

A lustrous light yellow-gold, Prismatic-like specimen of  $C_{24}H_{15}Cl_3$ , approximate dimensions 0.588 mm x 0.769 mm x 0.954 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Quest system equipped with ( $\lambda = 0.71076 \text{ \AA}$ ) a Mo monochromator.

**Table 1: Data collection details for 09122022DumuP1.**

Axis	dx/m m	2 $\theta$ / °	$\omega$ / °	$\phi$ / °	$\chi$ / °	Widt h/°	Fram es	Time /s	Wavelengt h/Å	Voltage /kV	Current/ mA	Temperatu re/K
Phi	34.96 7	1.7 3	- 11.0 2	0.00	54. 76	2.00	180	10.0 0	0.71076	50	20.0	n/a
Ome ga	34.96 7	47. 68	34.9 2	252. 00	54. 76	2.00	77	10.0 0	0.71076	50	20.0	n/a
Ome ga	34.96 7	47. 68	34.9 2	108. 00	54. 76	2.00	77	10.0 0	0.71076	50	20.0	n/a
Ome ga	34.96 7	1.7 3	- 165. 02	0.00	54. 76	2.00	77	10.0 0	0.71076	50	20.0	n/a
Ome ga	34.96 7	47. 68	34.9 2	36.0 0	54. 76	2.00	77	10.0 0	0.71076	50	20.0	n/a
Ome ga	34.96 7	47. 68	34.9 2	180. 00	54. 76	2.00	77	10.0 0	0.71076	50	20.0	n/a
Ome ga	34.96 7	1.7 3	- 165. 02	- 72.0 0	54. 76	2.00	77	10.0 0	0.71076	50	20.0	n/a
Phi	49.96 7	0.0 0	0.00	0.00	54. 76	1.00	180	1.00	0.71076	50	20.0	n/a

A total of 822 frames were collected. The total exposure time was 1.83 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 55429 reflections to a maximum  $\theta$  angle of 27.94° (0.76 Å resolution), of which 4646 were independent (average redundancy 11.930, completeness = 99.8%,  $R_{\text{int}} = 4.42\%$ ,  $R_{\text{sig}} = 1.72\%$ ) and 3927 (84.52%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $\underline{a} = 10.0711(3)$  Å,  $\underline{b} = 10.8430(4)$  Å,  $\underline{c} = 11.0794(4)$  Å,  $\alpha = 110.748(2)^\circ$ ,  $\beta = 99.407(2)^\circ$ ,  $\gamma = 113.569(2)^\circ$ , volume = 969.11(6) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 9818 reflections above  $20\sigma(I)$  with  $4.627^\circ < 2\theta < 55.77^\circ$ . Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.925.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group  $P -1$ , with  $Z = 2$  for the formula unit,  $C_{24}H_{15}Cl_3$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 290 variables converged at  $R1 = 3.29\%$ , for the observed data and  $wR2 = 9.44\%$  for all data. The goodness-of-fit was 1.063. The largest peak in the final difference electron density synthesis was  $0.260 e^-/\text{\AA}^3$  and the largest hole was  $-0.334 e^-/\text{\AA}^3$  with an RMS deviation of  $0.040 e^-/\text{\AA}^3$ . On the basis of the final model, the calculated density was  $1.404 \text{ g/cm}^3$  and  $F(000)$ , 420  $e^-$ .

**Table 2. Sample and crystal data for 09122022DumuP1.**

<b>Identification code</b>	09122022DumuP1	
<b>Chemical formula</b>	$C_{24}H_{15}Cl_3$	
<b>Formula weight</b>	409.71 g/mol	
<b>Temperature</b>	293(2) K	
<b>Wavelength</b>	0.71076 $\text{\AA}$	
<b>Crystal size</b>	0.588 x 0.769 x 0.954 mm	
<b>Crystal habit</b>	lustrous light yellow-gold Prismatic	
<b>Crystal system</b>	triclinic	
<b>Space group</b>	P -1	
<b>Unit cell dimensions</b>	$a = 10.0711(3) \text{\AA}$	$\alpha = 110.748(2)^\circ$
	$b = 10.8430(4) \text{\AA}$	$\beta = 99.407(2)^\circ$
	$c = 11.0794(4) \text{\AA}$	$\gamma = 113.569(2)^\circ$
<b>Volume</b>	$969.11(6) \text{\AA}^3$	
<b>Z</b>	2	
<b>Density (calculated)</b>	$1.404 \text{ g/cm}^3$	
<b>Absorption coefficient</b>	$0.479 \text{ mm}^{-1}$	
<b>F(000)</b>	420	

**Table 3. Data collection and structure refinement for 09122022DumuP1.**

<b>Diffractometer</b>	D8 Quest	
<b>Theta range for data collection</b>	2.54 to 27.94°	
<b>Index ranges</b>	-13<=h<=13, -14<=k<=14, -14<=l<=14	
<b>Reflections collected</b>	55429	
<b>Independent reflections</b>	4646 [R(int) = 0.0442]	
<b>Coverage of independent reflections</b>	99.8%	
<b>Absorption correction</b>	Multi-Scan	
<b>Structure solution technique</b>	direct methods	
<b>Structure solution program</b>	XT, VERSION 2018/2	
<b>Refinement method</b>	Full-matrix least-squares on F <sup>2</sup>	
<b>Refinement program</b>	SHELXL-2019/1 (Sheldrick, 2019)	
<b>Function minimized</b>	$\Sigma w(F_o^2 - F_c^2)^2$	
<b>Data / restraints / parameters</b>	4646 / 0 / 290	
<b>Goodness-of-fit on F<sup>2</sup></b>	1.063	
<b><math>\Delta/\sigma_{\max}</math></b>	0.001	
<b>Final R indices</b>	3927 data; I>2σ(I)	R1 = 0.0329, wR2 = 0.0892
	all data	R1 = 0.0404, wR2 = 0.0944
<b>Weighting scheme</b>	w=1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> )+(0.0422P) <sup>2</sup> +0.3468P] where P=(F <sub>o</sub> <sup>2</sup> +2F <sub>c</sub> <sup>2</sup> )/3	

<b>Extinction coefficient</b>	0.0029(18)
<b>Largest diff. peak and hole</b>	0.260 and -0.334 eÅ <sup>-3</sup>
<b>R.M.S. deviation from mean</b>	0.040 eÅ <sup>-3</sup>

**Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å<sup>2</sup>) for 09122022DumuP1.**

U(eq) is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

	<b>x/a</b>	<b>y/b</b>	<b>z/c</b>	<b>U(eq)</b>
C11	0.70504(5)	0.87441(5)	0.81005(4)	0.05117(13)
C12	0.50547(5)	0.92388(4)	0.32886(5)	0.04858(12)
C13	0.60638(6)	0.39691(5)	0.02526(4)	0.05365(13)
C1	0.9975(2)	0.10361(18)	0.90886(16)	0.0456(4)
C2	0.1384(2)	0.18416(19)	0.90029(18)	0.0525(4)
C3	0.1644(2)	0.1339(2)	0.7784(2)	0.0515(4)
C4	0.90189(16)	0.91949(15)	0.66728(14)	0.0329(3)
C5	0.88070(17)	0.97228(16)	0.79314(14)	0.0353(3)
C6	0.77558(16)	0.78400(15)	0.53924(14)	0.0328(3)
C7	0.63638(16)	0.77919(16)	0.48957(14)	0.0337(3)
C8	0.51835(15)	0.65521(15)	0.36891(14)	0.0307(3)
C9	0.54080(16)	0.53477(16)	0.29854(14)	0.0327(3)
C10	0.67904(16)	0.53712(15)	0.34564(14)	0.0321(3)
C11	0.79681(16)	0.66323(16)	0.46613(14)	0.0343(3)
C12	0.69616(15)	0.40208(15)	0.27464(14)	0.0323(3)

	<b>x/a</b>	<b>y/b</b>	<b>z/c</b>	<b>U(eq)</b>
C13	0.74649(19)	0.34253(18)	0.35327(17)	0.0402(3)
C14	0.7575(2)	0.21303(19)	0.2927(2)	0.0468(4)
C15	0.7177(2)	0.13938(18)	0.1516(2)	0.0484(4)
C16	0.66911(19)	0.19581(18)	0.07100(18)	0.0446(4)
C17	0.65972(16)	0.32654(16)	0.13267(15)	0.0348(3)
C18	0.36580(15)	0.64389(16)	0.31753(13)	0.0310(3)
C19	0.04747(18)	0.00230(19)	0.66369(17)	0.0421(3)
C20	0.34788(17)	0.75851(17)	0.30154(15)	0.0368(3)
C21	0.2025(2)	0.7422(2)	0.2548(2)	0.0586(5)
C22	0.0717(2)	0.6093(3)	0.2219(3)	0.0708(6)
C23	0.0853(2)	0.4931(2)	0.2344(2)	0.0588(5)
C24	0.23019(18)	0.50969(19)	0.28144(17)	0.0411(3)

**Table 5. Bond lengths (Å) for 09122022DumuP1.**

C1-C5	1.7432(16)	C12-C20	1.7345(16)
C13-C17	1.7462(16)	C1-C2	1.377(3)
C1-C5	1.389(2)	C2-C3	1.378(3)
C3-C19	1.386(2)	C4-C5	1.395(2)
C4-C19	1.396(2)	C4-C6	1.4926(18)
C6-C7	1.3928(19)	C6-C11	1.3949(19)
C7-C8	1.3916(19)	C8-C9	1.3918(19)
C8-C18	1.4876(18)	C9-C10	1.3914(19)
C10-C11	1.3967(19)	C10-C12	1.4908(18)
C12-C17	1.392(2)	C12-C13	1.396(2)
C13-C14	1.384(2)	C14-C15	1.377(3)
C15-C16	1.377(3)	C16-C17	1.388(2)
C18-C20	1.391(2)	C18-C24	1.401(2)
C20-C21	1.387(2)	C21-C22	1.378(3)
C22-C23	1.371(3)	C23-C24	1.382(2)

**Table 6. Bond angles (°) for 09122022DumuP1.**

C2-C1-C5	119.59(16)	C1-C2-C3	120.34(15)
C2-C3-C19	119.65(17)	C5-C4-C19	117.00(13)
C5-C4-C6	122.79(13)	C19-C4-C6	120.18(13)
C1-C5-C4	121.66(15)	C1-C5-C11	117.64(13)
C4-C5-C11	120.69(11)	C7-C6-C11	119.34(12)

C7-C6-C4	119.97(12)	C11-C6-C4	120.67(12)
C8-C7-C6	120.85(12)	C7-C8-C9	118.97(12)
C7-C8-C18	121.85(12)	C9-C8-C18	119.08(12)
C10-C9-C8	121.30(12)	C9-C10-C11	118.92(12)
C9-C10-C12	120.33(12)	C11-C10-C12	120.58(12)
C6-C11-C10	120.62(13)	C17-C12-C13	116.95(13)
C17-C12-C10	124.25(13)	C13-C12-C10	118.76(13)
C14-C13-C12	121.54(15)	C15-C14-C13	120.02(16)
C14-C15-C16	120.01(15)	C15-C16-C17	119.63(16)
C16-C17-C12	121.83(15)	C16-C17-C13	117.18(12)
C12-C17-C13	120.96(11)	C20-C18-C24	116.99(13)
C20-C18-C8	124.17(13)	C24-C18-C8	118.84(13)
C3-C19-C4	121.72(16)	C21-C20-C18	121.60(15)
C21-C20-C12	116.70(13)	C18-C20-C12	121.59(11)
C22-C21-C20	119.79(18)	C23-C22-C21	120.08(17)
C22-C23-C24	120.08(17)	C23-C24-C18	121.45(16)

**Table 7. Torsion angles (°) for 09122022DumuP1.**

C5-C1-C2-C3	-0.9(3)	C1-C2-C3-C19	0.6(3)
C2-C1-C5-C4	-0.3(2)	C2-C1-C5-Cl1	179.72(13)
C19-C4-C5-C1	1.7(2)	C6-C4-C5-C1	- 176.29(14)
C19-C4-C5-Cl1	- 178.26(11)	C6-C4-C5-Cl1	3.70(19)
C5-C4-C6-C7	56.5(2)	C19-C4-C6-C7	- 121.51(16)
C5-C4-C6-C11	- 125.31(16)	C19-C4-C6-C11	56.7(2)
C11-C6-C7-C8	0.5(2)	C4-C6-C7-C8	178.74(13)
C6-C7-C8-C9	0.5(2)	C6-C7-C8-C18	176.90(13)
C7-C8-C9-C10	-0.8(2)	C18-C8-C9-C10	- 177.32(13)
C8-C9-C10-C11	0.1(2)	C8-C9-C10-C12	175.40(13)
C7-C6-C11-C10	-1.2(2)	C4-C6-C11-C10	- 179.41(14)
C9-C10-C11-C6	0.9(2)	C12-C10-C11- C6	- 174.39(14)
C9-C10-C12- C17	50.0(2)	C11-C10-C12- C17	- 134.81(15)
C9-C10-C12- C13	- 127.57(15)	C11-C10-C12- C13	47.6(2)
C17-C12-C13- C14	-0.9(2)	C10-C12-C13- C14	176.82(14)
C12-C13-C14- C15	-0.3(3)	C13-C14-C15- C16	1.0(3)

C14-C15-C16- C17	-0.4(3)	C15-C16-C17- C12	-0.9(2)
C15-C16-C17- C13	176.96(13)	C13-C12-C17- C16	1.5(2)
C10-C12-C17- C16	- 176.07(14)	C13-C12-C17- C13	- 176.25(11)
C10-C12-C17- C13	6.2(2)	C7-C8-C18-C20	50.3(2)
C9-C8-C18-C20	- 133.28(15)	C7-C8-C18-C24	- 130.21(16)
C9-C8-C18-C24	46.22(19)	C2-C3-C19-C4	0.9(3)
C5-C4-C19-C3	-2.1(2)	C6-C4-C19-C3	176.02(15)
C24-C18-C20- C21	1.4(2)	C8-C18-C20- C21	- 179.13(16)
C24-C18-C20- C12	- 174.62(11)	C8-C18-C20-C12	4.9(2)
C18-C20-C21- C22	-0.6(3)	C12-C20-C21- C22	175.56(18)
C20-C21-C22- C23	-0.5(4)	C21-C22-C23- C24	0.7(4)
C22-C23-C24- C18	0.1(3)	C20-C18-C24- C23	-1.1(2)
C8-C18-C24- C23	179.37(16)		

**Table 8. Anisotropic atomic displacement parameters ( $\text{\AA}^2$ ) for 09122022DumuP1.**

The anisotropic atomic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

	<b>U<sub>11</sub></b>	<b>U<sub>22</sub></b>	<b>U<sub>33</sub></b>	<b>U<sub>23</sub></b>	<b>U<sub>13</sub></b>	<b>U<sub>12</sub></b>
C1	0.0505(2)	0.0497(2)	0.0419(2)	0.01732(18)	0.01703(17)	0.01811(19)
C12	0.0485(2)	0.0382(2)	0.0576(3)	0.02418(18)	0.01671(18)	0.01936(17)
C13	0.0696(3)	0.0592(3)	0.0358(2)	0.01915(18)	0.01447(18)	0.0393(2)
C1	0.0546(9)	0.0355(8)	0.0297(7)	0.0074(6)	0.0021(7)	0.0193(7)
C2	0.0475(9)	0.0340(8)	0.0420(9)	0.0072(7)	-0.0078(7)	0.0088(7)
C3	0.0351(8)	0.0455(9)	0.0537(10)	0.0204(8)	0.0023(7)	0.0099(7)
C4	0.0340(7)	0.0285(6)	0.0300(6)	0.0094(5)	0.0021(5)	0.0172(5)
C5	0.0391(7)	0.0290(7)	0.0308(7)	0.0107(5)	0.0047(6)	0.0164(6)
C6	0.0327(7)	0.0304(7)	0.0270(6)	0.0082(5)	0.0045(5)	0.0153(6)
C7	0.0363(7)	0.0318(7)	0.0284(6)	0.0078(5)	0.0072(5)	0.0201(6)
C8	0.0290(6)	0.0319(7)	0.0294(6)	0.0121(5)	0.0080(5)	0.0163(5)
C9	0.0297(6)	0.0283(6)	0.0303(7)	0.0072(5)	0.0059(5)	0.0131(5)
C10	0.0333(7)	0.0293(6)	0.0304(6)	0.0094(5)	0.0098(5)	0.0171(5)
C11	0.0317(7)	0.0337(7)	0.0321(7)	0.0098(6)	0.0058(5)	0.0184(6)
C12	0.0281(6)	0.0280(6)	0.0344(7)	0.0089(5)	0.0095(5)	0.0138(5)
C13	0.0450(8)	0.0397(8)	0.0394(8)	0.0170(7)	0.0157(7)	0.0248(7)
C14	0.0490(9)	0.0397(8)	0.0619(11)	0.0273(8)	0.0222(8)	0.0267(7)
C15	0.0491(9)	0.0293(7)	0.0616(11)	0.0129(7)	0.0213(8)	0.0216(7)
C16	0.0434(8)	0.0329(8)	0.0416(8)	0.0039(6)	0.0137(7)	0.0172(7)

	<b>U<sub>11</sub></b>	<b>U<sub>22</sub></b>	<b>U<sub>33</sub></b>	<b>U<sub>23</sub></b>	<b>U<sub>13</sub></b>	<b>U<sub>12</sub></b>
C17	0.0308(6)	0.0303(7)	0.0344(7)	0.0092(6)	0.0087(5)	0.0135(5)
C18	0.0296(6)	0.0349(7)	0.0262(6)	0.0110(5)	0.0088(5)	0.0172(5)
C19	0.0374(8)	0.0449(8)	0.0379(8)	0.0163(7)	0.0063(6)	0.0204(7)
C20	0.0345(7)	0.0379(7)	0.0374(7)	0.0159(6)	0.0112(6)	0.0194(6)
C21	0.0466(10)	0.0598(11)	0.0796(14)	0.0358(10)	0.0144(9)	0.0353(9)
C22	0.0320(9)	0.0772(14)	0.0984(17)	0.0392(13)	0.0106(10)	0.0290(9)
C23	0.0295(8)	0.0551(11)	0.0753(13)	0.0262(10)	0.0133(8)	0.0121(8)
C24	0.0348(7)	0.0392(8)	0.0456(8)	0.0184(7)	0.0141(6)	0.0163(6)

**Table 9. Hydrogen atomic coordinates and isotropic atomic displacement parameters ( $\text{\AA}^2$ ) for 09122022DumuP1.**

	x/a	y/b	z/c	U(eq)
H1	0.647(2)	0.150(2)	-0.021(2)	0.062000
H2	0.724(2)	0.056(3)	0.117(2)	0.062000
H3	0.794(2)	0.176(2)	0.352(2)	0.062000
H4	0.771(2)	0.391(2)	0.449(2)	0.062000
H5	0.461(2)	0.451(2)	0.217(2)	0.062000
H6	0.896(3)	0.668(2)	0.500(2)	0.062000
H7	0.622(2)	0.857(2)	0.536(2)	0.062000
H8	1.065(2)	0.972(2)	0.580(2)	0.062000
H9	1.257(3)	1.185(2)	0.770(2)	0.062000
H10	1.213(2)	1.276(2)	0.982(2)	0.062000
H11	0.978(2)	1.136(2)	0.992(2)	0.062000
H12	0.232(2)	0.424(3)	0.291(2)	0.062000
H13	-0.004(3)	0.401(2)	0.214(2)	0.062000
H14	-0.028(3)	0.598(2)	0.187(2)	0.062000
H15	0.197(2)	0.822(2)	0.242(2)	0.062000