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Supplementary Material

A Simple, One-Pot Synthesis of *Trans*-Substituted Spiro[5,5]undecane-1,5,9-triones with Aromatic Aldehydes and Meldrum's Acid as the Starting Materials

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General Methods.

The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400M and 100M, respectively. The chemical shifts were reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. The coupling constants *J* were given in Hz. The conformational analysis of **2a** were performed by the Spartan'10 package using the MMFF94s molecular mechanics force field with a Systematic and Monte Carlo search. All possible conformers were searched, considering the degrees of freedom of the system and retaining only 2 structures within an energy range of 10 kcal/mol with respect to the most stable conformer. All MM sorted conformations were further fully subjected to *ab initio* energy minimization as implemented in the Gaussian09[i] package. NMR chemical shifts[ii] (including TMS reference) were computed at the B3LYP[iii]/6-311++G(2d,2p)[iv]/PCM(solvent=chloroform) level of theory. For **2a**, the NMR parameters were averaged on the basis of the Boltzmann distribution of the optimized conformers derived from the relative enthalpies. Flash chromatography (FC) was performed using silica gel. Electrospray ionization (ESI) mass spectrometry was performed on an API 100 Perkin-Elmer SCIEX single quadrupole mass spectrometer. High-resolution mass spectra (HRMS) were recorded on an Agilent Technologies 6530 accurate-mass Q-TOF LC/MS using ESI(electrospray ionization). The diffraction data was collected at 293 K with an Oxford Diffraction Xcalibur Nova diffractometer system. For thin-layer chromatography (TLC), silica gel plates F254 were used and compounds were visualized by irradiation with UV light. All solvents and commercially available chemicals were used as received.

X-Ray diffraction study:

The diffraction data of complex **2a** was collected at 293(2) K with an Oxford Diffraction Xcalibur Nova diffractometer system using CuKα (λ = 1.5418 Å) radiation with the ω scan mode. The structure was solved by the direct methods and refined by full-matrix least-squares refinements based on *F*. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms added to their geometrically ideal positions and refined isotropically. Crystal dada for **2a**: $C_{23}H_{22}O_5$, Mr = 378.41, tetragonal , *P*-41212, a = 7.61176(6), b = 7.61176(6), c = 33.3638(4) Å, α = 90.0°, β = 90.0°, γ =90.0°, V = 1933.06(10) Å^3, *Z*=4, D_c= 1.300 g/cm^3, μ = 0.745 mm^{-1}, 18313 reflections measured, 1867 uniqe, final $R(F^2)$=0.0515 using 10870 reflections with $I > 2.0\sigma(I)$, *R*(all data)=0.0533, CCDC 791513.

The final atomic coordinates, and crystallographic data for molecules **2a** have been deposited to the Cambridge Crystallographic Data Centre, 12 Union Road, CB2 1EZ, UK (Telephone: (44) 01223 762910, Facsimile: (44) 01223 336033; e-mail: deposit@ccdc.cam.ac.uk) and are available on request quoting the deposition number CCDC 791513 for **2a**(Figure 1).

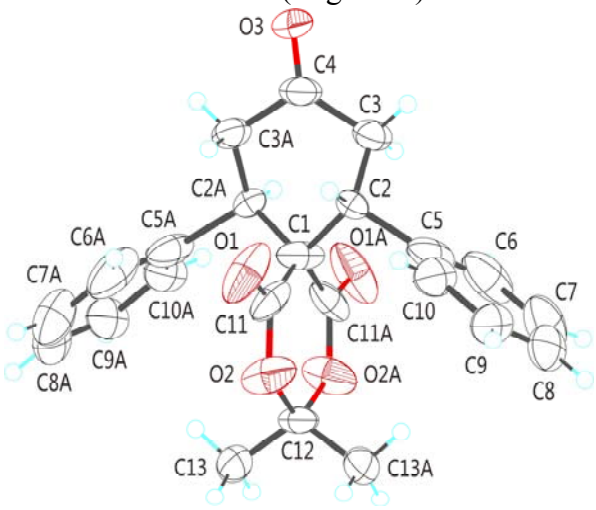

Figure 1 ORTEP of the trans-substituted spiro[5,5]undecane-1,5,9-triones (**2a**) (CCDC 791513)

Table 1 Computed[a] and Experimental[b] ^{1}H and ^{13}C NMR Chemical Shifts (ppm, relative to TMS) for **2a**; For atom labelling, see Figure 1**.**

Atom no.	Thery δH	Exptl. δH	Error δH	Thery δC	Exptl. δC	Error δC
C1	-	-	-	67.86	60.57	7.29
C2/C2A	3.87,4.22	3.65	0.22,0.57	48.94,59.04	50.08	-1.14,8.96
C3/C3A	2.64,2.70	2.57	0.07,0.13	47.79,50.75	42.85	4.94,7.9
	3.63,4.04	3.94	-0.31,0.10			
C4	-	-	-	222.08	207.56	14.52
C5/C5A	-	-	-	147.72,148.51	137.12	10.6,11.39
C6-C10 &	7.84	8.54-6.22(m,10H)	-0.7-1.32	138.60	129.20	-9.4-(-5.63)

C6A-C10A	**7.83**			**136.24**	**128.99**	
	7.70			**135.68**	**128.68**	
	7.69			**134.89**	**128.47**	
	7.65			**134.88**		
	7.61			**134.81**		
	7.57			**134.39**		
	7.57			**134.37**		
	7.54			**134.26**		
	7.54			**134.10**		
C11/C11A	**-**	**-**	**-**	**176.59,178.55**	**165.26,168.18**	**11.33,10.37**
C12	**-**	**-**	**-**	**113.65**	**106.36**	**7.29**
C13/C13A	**1.85**	**0.48**	**1.37**	**29.50,32.01**	**28.30**	**1.2,3.71**
	1.66		**1.18**			
	1.63		**1.15**			
	1.34		**0.86**			
	1.26		**0.78**			
	-0.04		**-0.52**			

[a]Boltzmann average over 2 conformers (B3LYP/6-311++G(2d,2p)/PCM(solvent=chloroform)),[b]Measured at 400MHz(^{1}H) and 100 MHz(^{13}C) in $CDCl_3$.

Characterization of compounds 2a-o

7,11-Bisphenyl-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trione (2a)
Yield: 144mg, 76%, mp 199–201^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 – 6.22 (m, 10H), 3.94 (dd, *J* = 14.4, 4.3 Hz, 2H), 3.65 (t, *J* = 14.7 Hz, 2H), 2.57 (dd, *J* = 15.2, 4.5 Hz, 2H), 0.48 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.56, 168.18, 165.26, 137.12, 129.20, 128.99, 128.68, 128.47, 106.36, 77.36, 77.05, 76.73, 60.57, 50.08, 42.85, 28.30. HRMS (ESI-TOF) calcd for $C_{23}H_{21}O_5^-$[M-H]$^-$ 377.1389, found 377.1401

7,11-Bis-(4-fluorophenyl)-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trione (2b)
Yield: 120mg, 58%, mp 155–156^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (dd, *J* = 8.7, 5.3 Hz, 4H), 7.04 (t, *J* = 8.6 Hz, 4H), 3.99 (dd, *J* = 14.4, 4.3 Hz, 2H), 3.65 (t, *J* = 14.7 Hz, 2H), 2.63 (dd, *J* = 14.8, 4.3 Hz, 2H), 0.66 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 206.71, 168.14, 165.19, 163.95, 161.47, 132.91, 132.88, 130.27, 130.18, 116.29, 116.08, 106.49, 77.33, 77.01, 76.69, 60.62, 49.28, 42.97, 28.52. HRMS (ESI-TOF) calcd for $C_{23}H_{19}F_2O_5^-$[M-H]$^-$ 413.1201, found 413.1205

7,11-Bis-(4-chlorophenyl)-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trione (2c)
Yield: 147mg, 66%, mp 176–178^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.2 Hz, 4H), 7.17 (d, *J* = 8.4 Hz, 4H), 3.98 (dd, *J* = 14.4, 4.3 Hz, 2H), 3.64 (t, *J* = 14.6 Hz, 2H), 2.62 (dd, *J* = 14.8, 4.2 Hz, 2H), 0.68 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 206.43, 167.96, 165.05, 135.43, 134.81, 131.39, 129.84, 129.40, 129.10, 106.58, 77.35, 77.03, 76.72, 60.27, 49.41, 42.71, 28.55. HRMS (ESI-TOF) calcd for $C_{23}H_{19}$

$Cl_2O_5^-$[M-H]$^-$ 445.0610, found 445.0613

7,11-Bis-(4-bromophenyl)-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trione (2d)

Yield: 160mg, 60%, mp 182–184^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.4 Hz, 4H), 7.11 (d, *J* = 8.4 Hz, 4H), 3.97 (dd, *J* = 14.3, 4.2 Hz, 2H), 3.64 (t, *J* = 14.7 Hz, 2H), 2.63 (dd, *J* = 14.9, 4.1 Hz, 2H), 0.68 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 206.39, 167.93, 165.03, 135.91, 132.40, 130.14, 122.89, 106.62, 77.33, 77.01, 76.70, 60.14, 49.51, 42.65, 28.56. HRMS (ESI-TOF) calcd for $C_{23}H_{19}Br_2O_5^-$[M-H]$^-$ 534.9579, found 534.9586

7,11-Bis-(4-methylphenyl)-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trion e (2e)

Yield: 158mg, 78%, mp 185–186^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 – 7.01 (m, 8H), 3.96 (dd, *J* = 14.3, 4.3 Hz, 2H), 3.69 (t, *J* = 14.7 Hz, 2H), 2.61 (dd, *J* = 15.1, 4.4 Hz, 2H), 2.29 (s, 6H), 0.59 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.93, 168.31, 165.37, 138.47, 134.16, 129.75, 128.30, 106.27, 77.35, 77.03, 76.72, 60.70, 49.71, 43.00, 28.33, 20.98. HRMS (ESI-TOF) calcd for $C_{23}H_{25}O_5^-$[M-H]$^-$ 405.1702, found 405.1710

7,11-Bis-(4-*t*-butylphenyl)-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trione (2f)

Yield: 206mg, 84%, mp 188–189^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.2 Hz, 4H), 7.16 (d, *J* = 8.3 Hz, 4H), 3.99 (dd, *J* = 14.3, 4.1 Hz, 2H), 3.71 (t, *J* = 14.6 Hz, 2H), 2.64 (dd, *J* = 14.8, 4.1 Hz, 2H), 1.25 (s, 18H), 0.50 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 208.06, 168.34, 165.28, 151.87, 134.09, 128.04, 126.05, 106.23, 77.33, 77.01, 76.69, 60.95, 49.52, 42.77, 34.51, 31.14, 28.08. HRMS (ESI-TOF) calcd for $C_{31}H_{37}O_5^-$[M-H]$^-$ 489.2641, found 489.2649

7,11-Bis-(4-methoxyphenyl)-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trio ne (2g)

Yield: 175mg, 80%, mp 183–185^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.7 Hz, 4H), 6.85 (d, *J* = 8.7 Hz, 4H), 3.95 (dd, *J* = 14.4, 4.3 Hz, 2H), 3.76 (s, 6H), 3.65 (t, *J* = 14.7 Hz, 2H), 2.60 (dd, *J* = 14.9, 4.3 Hz, 2H), 0.65 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.81, 168.48, 165.49, 159.69, 129.54, 129.25, 114.45, 106.30, 77.35, 77.03, 76.72, 60.96, 55.32, 49.28, 43.18, 28.51. HRMS (ESI-TOF) calcd for $C_{25}H_{25}O_7^-$[M-H]$^-$ 437.1600, found 437.1601

7,11-Bis-(4-nitrophenyl)-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trione (2h)

Yield: 134mg, 55%, mp 198–200^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 – 8.14 (m, 4H), 7.53 – 7.37 (m, 4H), 4.15 (dd, *J* = 14.3, 4.3 Hz, 2H), 3.72 (t, *J* = 14.7 Hz, 2H), 2.70 (dd, *J* = 15.3, 4.5 Hz, 2H), 0.63 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 204.61, 148.12, 143.59, 129.74, 124.39, 106.82, 77.32, 77.00, 76.68, 59.57, 49.82, 42.36,

28.72. LC/MS (ESI) m/z $[(M-H)]^-$= 487

7,11-Bis-(2-nitrophenyl)-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trione (2i)

Yield: 105mg, 43%, mp 153–155°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.70 – 7.52 (m, 4H), 7.52 – 7.42 (m, 2H), 4.80 (dd, *J* = 13.9, 4.7 Hz, 2H), 3.55 (m, 2H), 2.89 (dd, *J* = 16.3, 4.4 Hz, 2H), 0.73 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 204.10, 166.93, 166.05, 150.77, 132.91, 130.93, 129.61, 128.78, 125.49, 106.66, 77.32, 77.01, 76.69, 58.67, 43.23, 42.76, 28.53. LC/MS (ESI) m/z $[(M-H)]^-$= 487

7,11-Bis-(2-methylphenyl)-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trion e (2j)

Yield: 142mg, 70%, mp 185–186°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.23 – 7.04 (m, 6H), 4.33 (dd, *J* = 14.2, 4.5 Hz, 2H), 3.83 – 3.43 (m, 2H), 2.59 (dd, *J* = 16.0, 4.6 Hz, 2H), 2.36 (s, 6H), 0.79 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.80, 167.75, 166.78, 136.90, 136.18, 131.67, 128.19, 126.97, 126.72, 106.59, 77.34, 77.02, 76.70, 57.65, 45.44, 44.59, 28.57, 19.53. LC/MS (ESI) m/z $[(M-H)]^-$= 405

7,11-Bis-(3-nitrophenyl)-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trione (2k)

Yield: 124mg, 51%, mp 200–202°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 – 8.16 (m, 2H), 8.12 (s, 2H), 7.66 – 7.52 (m, 4H), 4.16 (dd, *J* = 14.4, 4.3 Hz, 2H), 3.75 (t, *J* = 14.7 Hz, 2H), 2.72 (dd, *J* = 15.1, 4.3 Hz, 2H), 0.62 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 204.70, 167.42, 164.56, 148.68, 138.90, 134.60, 130.49, 123.90, 123.41, 106.66, 77.36, 77.04, 76.73, 59.89, 49.63, 42.47, 28.58. LC/MS (ESI) m/z $[(M-H)]^-$= 487

7,11-Bis-(3,5-dimethoxyphenyl)-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trione (2l)

Yield: 127mg, 51%, mp 174–175°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 (s, 6H), 3.91 (dd, *J* = 14.3, 4.2 Hz, 2H), 3.75 (s, 12H), 3.65 (t, *J* = 14.7 Hz, 2H), 2.64 (dd, *J* = 15.1, 4.3 Hz, 2H), 0.78 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.45, 168.22, 165.38, 161.24, 139.18, 106.39, 106.33, 100.81, 77.32, 77.00, 76.69, 60.00, 55.43, 50.42, 42.94, 28.53. LC/MS (ESI) m/z $[(M-H)]^-$= 497

7,11-Bis-(1-naphthyl)-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trione (2m)

Yield: 124mg, 52%, mp 180–181°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.7 Hz, 0H), 7.82 (dd, *J* = 7.4, 4.9 Hz, 1H), 7.72 – 7.59 (m, 1H), 7.49 (dd, *J* = 16.5, 8.2 Hz, 1H), 5.16 (dd, *J* = 14.0, 3.9 Hz, 2H), 3.93 (t, *J* = 14.7 Hz, 2H), 2.80 (dd, *J* = 15.1, 3.8 Hz, 2H), 0.47 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.82, 167.19, 166.58,

134.13, 134.06, 130.92, 129.29, 128.71, 126.93, 126.29, 125.51, 125.17, 123.20, 106.38, 77.35, 77.03, 76.71, 58.87, 45.09, 43.70, 28.44. LC/MS (ESI) m/z $[(M-H)]^-$ = 477

7,11-Bis-(2-naphthyl)-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trione (2n)

Yield: 120mg, 50%, mp 221–223^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 – 7.76 (m, 6H), 7.73 (s, 2H), 7.54 – 7.43 (m, 4H), 7.37 (dd, *J* = 8.6, 1.8 Hz, 2H), 4.25 (dd, *J* = 14.3, 4.3 Hz, 2H), 3.90 (t, *J* = 14.7 Hz, 2H), 2.76 (dd, *J* = 15.1, 4.4 Hz, 2H), 0.29 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.49, 168.28, 165.55, 134.41, 133.23, 133.04, 129.02, 128.19, 127.97, 127.54, 126.69, 126.66, 125.67, 106.36, 77.34, 77.02, 76.70, 60.44, 50.42, 43.19, 28.27. LC/MS (ESI) m/z $[(M-H)]^-$ = 477

7,11-Bisferrocenyl-3,3-dimethyl-2,4-dioxaspiro-[5.5]undecane-1,5,9-trione (2o)

Yield: 178mg, 60%, decomposed at mp; ^1H NMR (400 MHz, $CDCl_3$): δ 4.09 (s, 10H), 4.07 – 4.03 (m, 6H), 3.99 – 3.96 (m, 2H), 3.56 (dd, *J* = 14.0, 4.5 Hz, 2H), 3.24 (t, *J* = 14.8 Hz, 2H), 2.95 (dd, *J* = 15.5, 4.4 Hz, 2H), 0.79 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 208.76, 169.26, 165.12, 106.46, 85.77, 77.37, 77.05, 76.74, 69.66, 69.27, 68.93, 68.60, 68.27, 66.21, 61.97, 44.76, 43.20, 28.91. LC/MS (ESI) m/z $[(M-H)]^-$ = 593

Copies of spectra

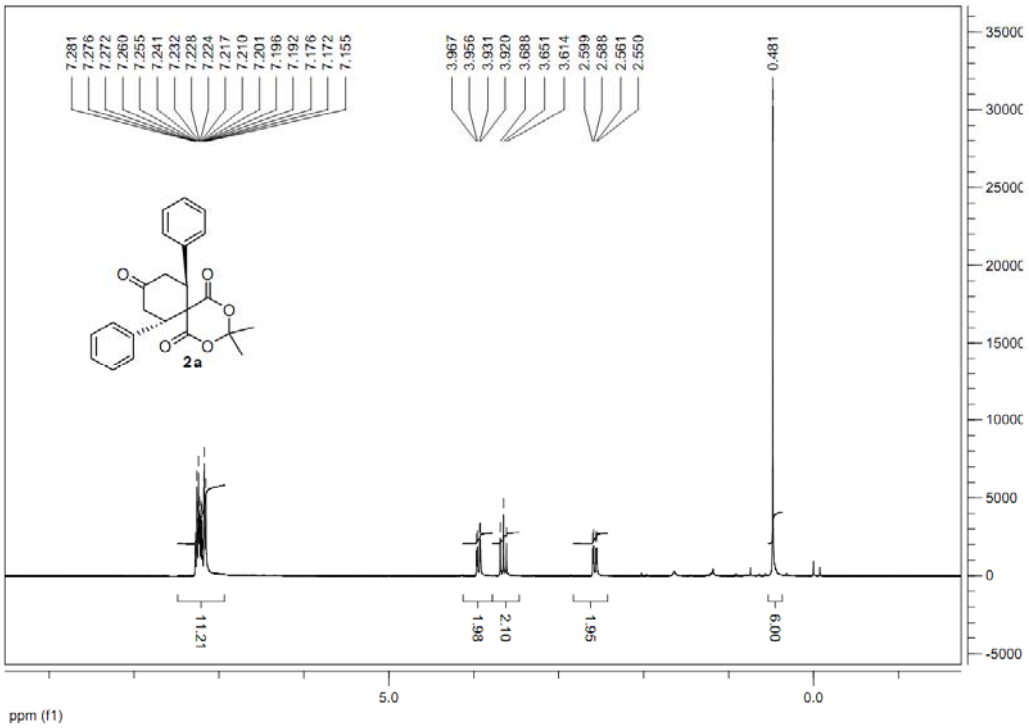

Figure 1. ^{1}H NMR spectrum ($CDCl_3$) of 2a

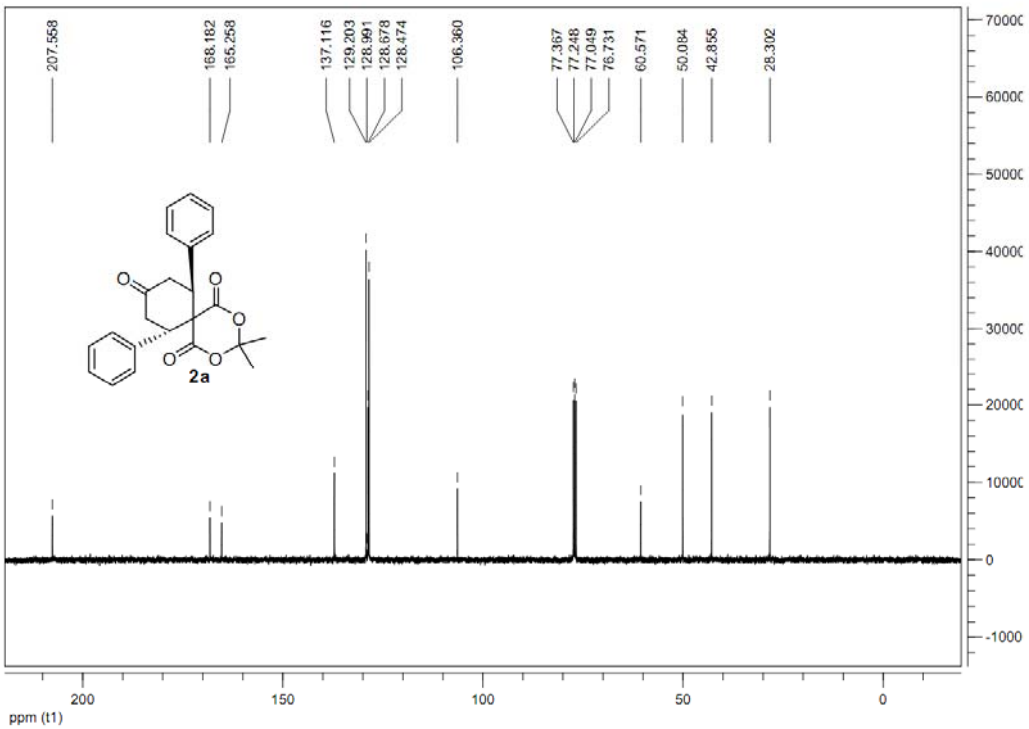

Figure 2. ^{13}C NMR spectrum ($CDCl_3$) of 2a

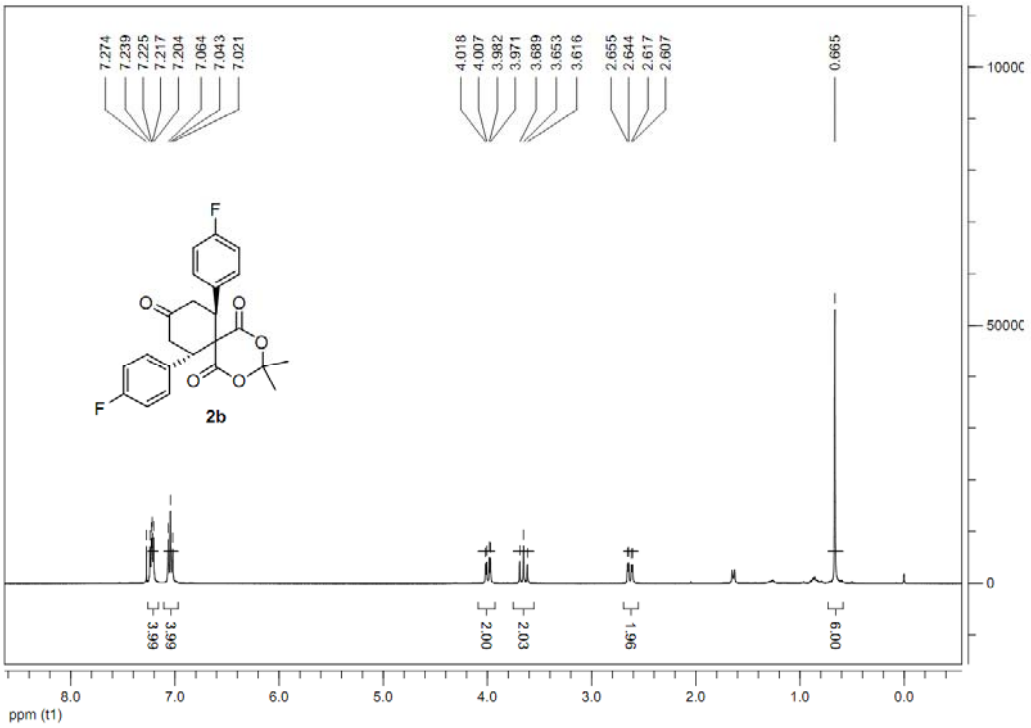

Figure 3. ^{1}H NMR spectrum ($CDCl_3$) of 2b

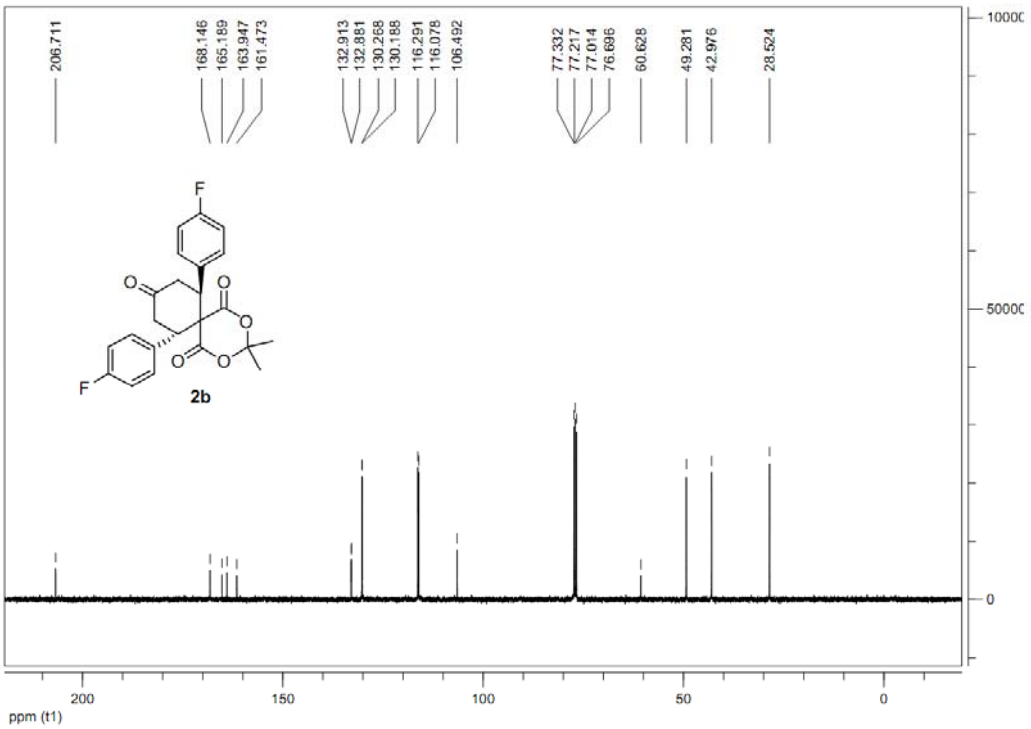

Figure 4. ^{13}C NMR spectrum ($CDCl_3$) of 2b

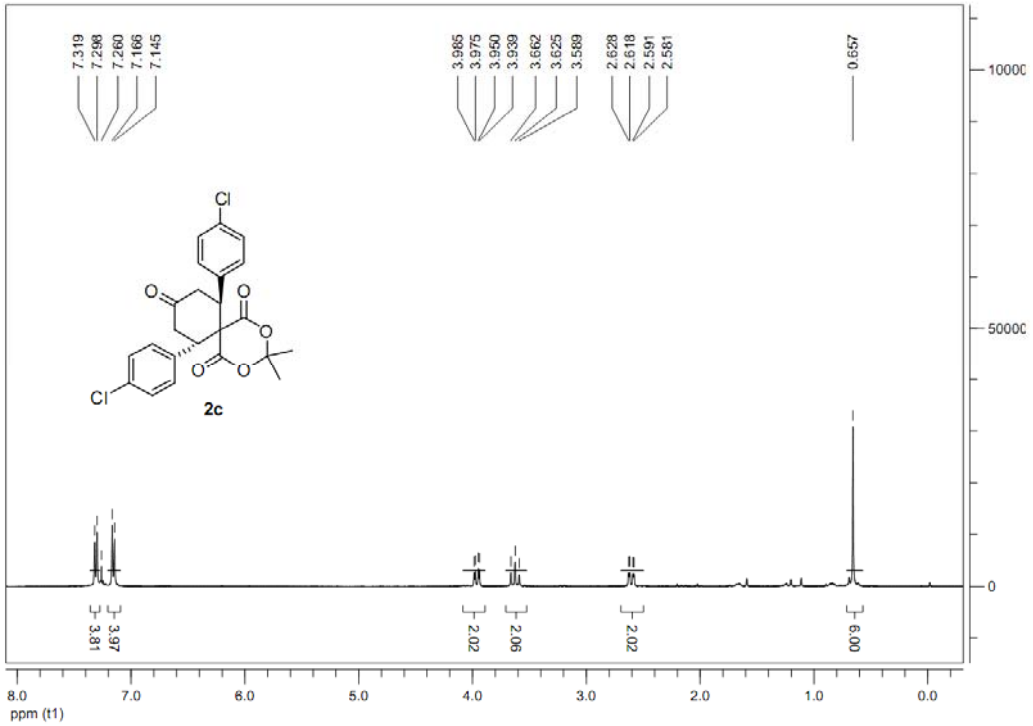

Figure 5. ^{1}H NMR spectrum ($CDCl_3$) of 2c

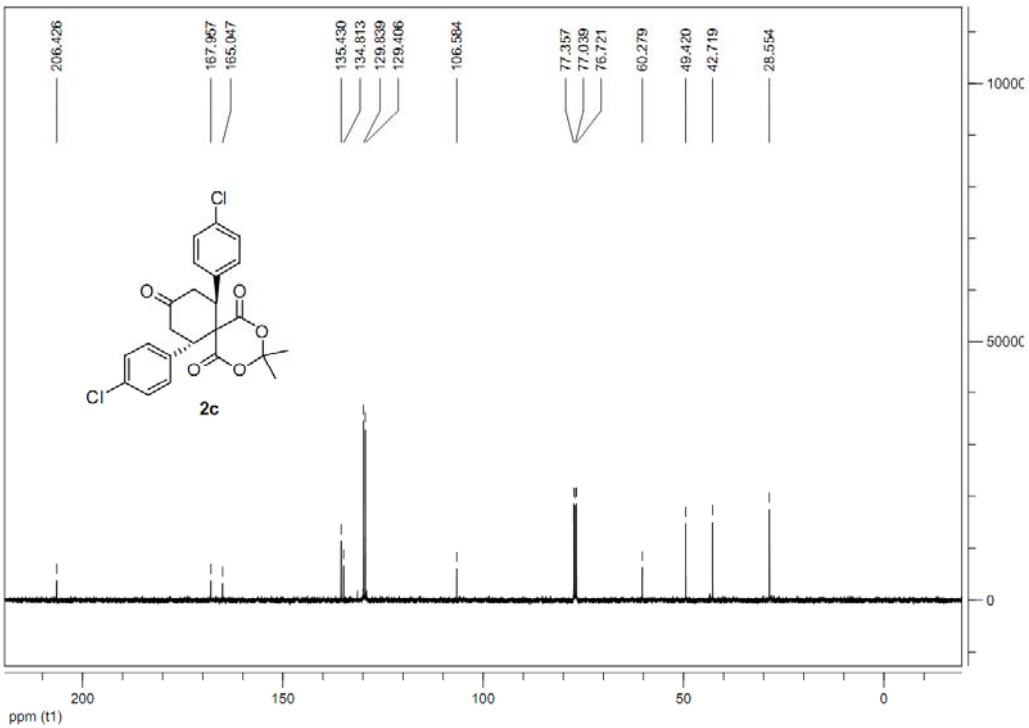

Figure 6. ^{13}C NMR spectrum ($CDCl_3$) of 2c

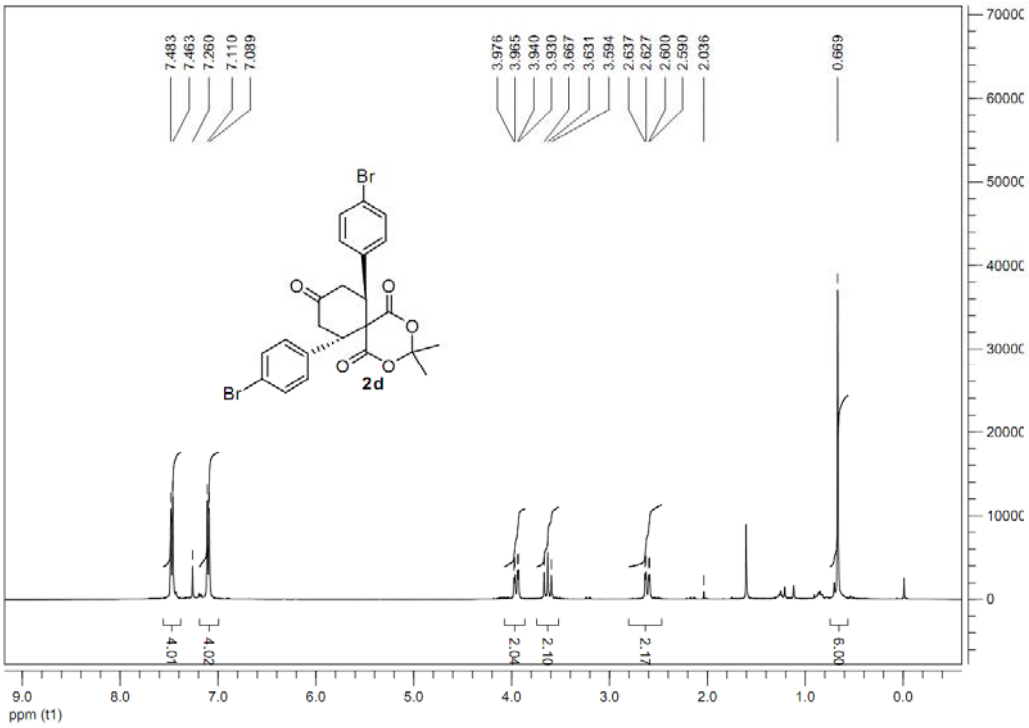

Figure 7. ^{1}H NMR spectrum ($CDCl_3$) of 2d

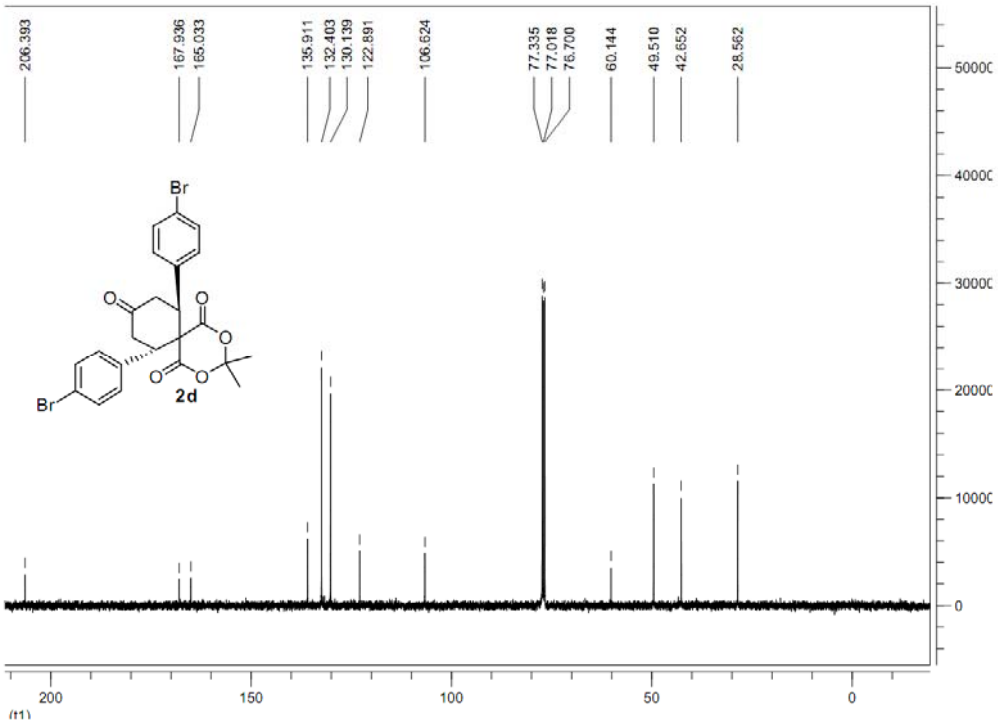

Figure 8. ^{13}C NMR spectrum ($CDCl_3$) of 2d

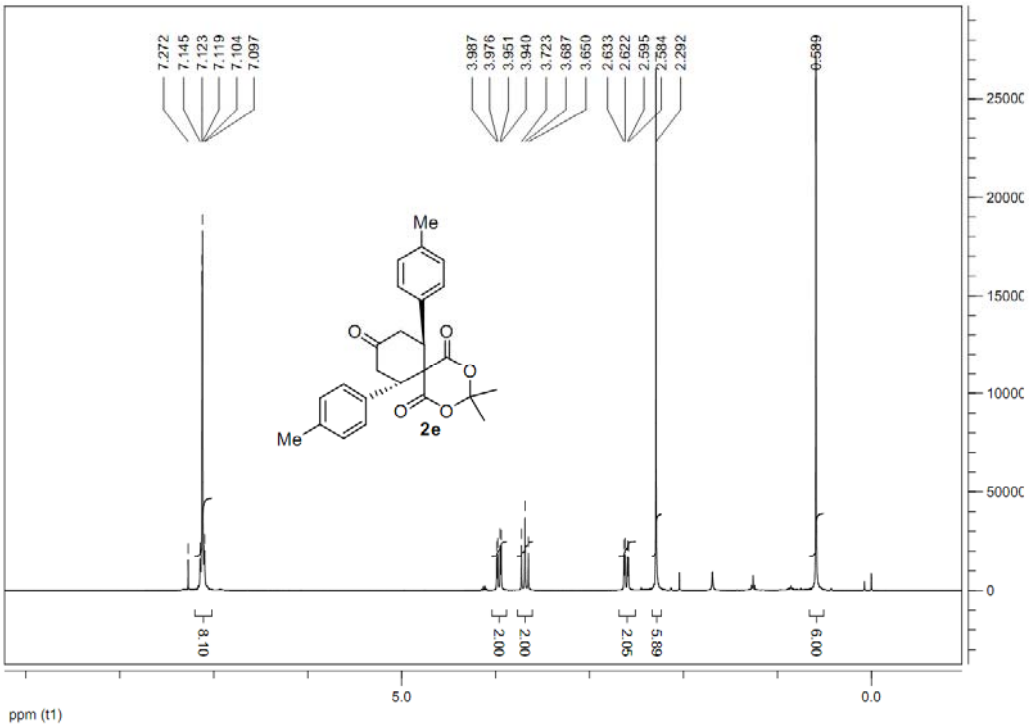

Figure 9. ^{1}H NMR spectrum ($CDCl_3$) of 2e

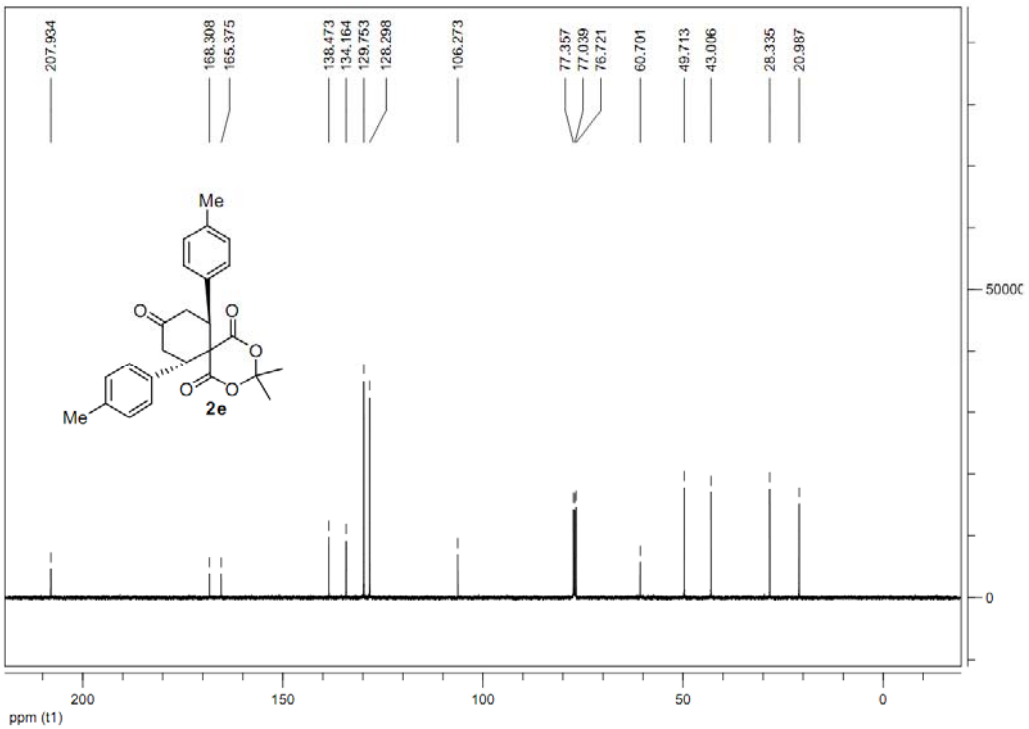

Figure 10. ^{13}C NMR spectrum ($CDCl_3$) of 2e

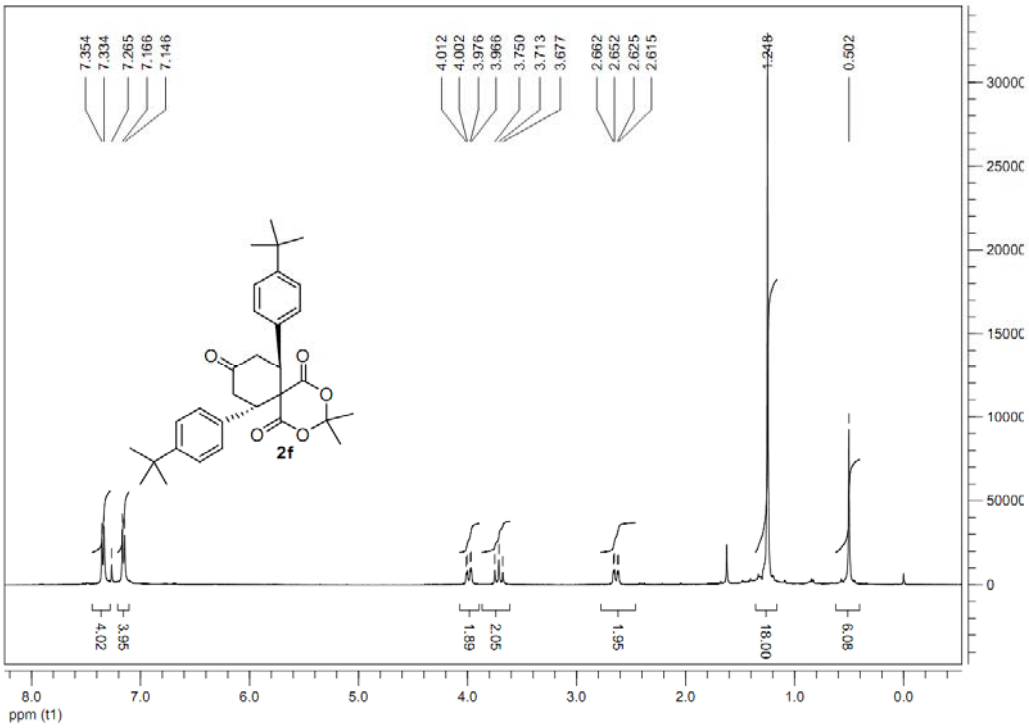

Figure 11. ^{1}H NMR spectrum ($CDCl_3$) of 2f

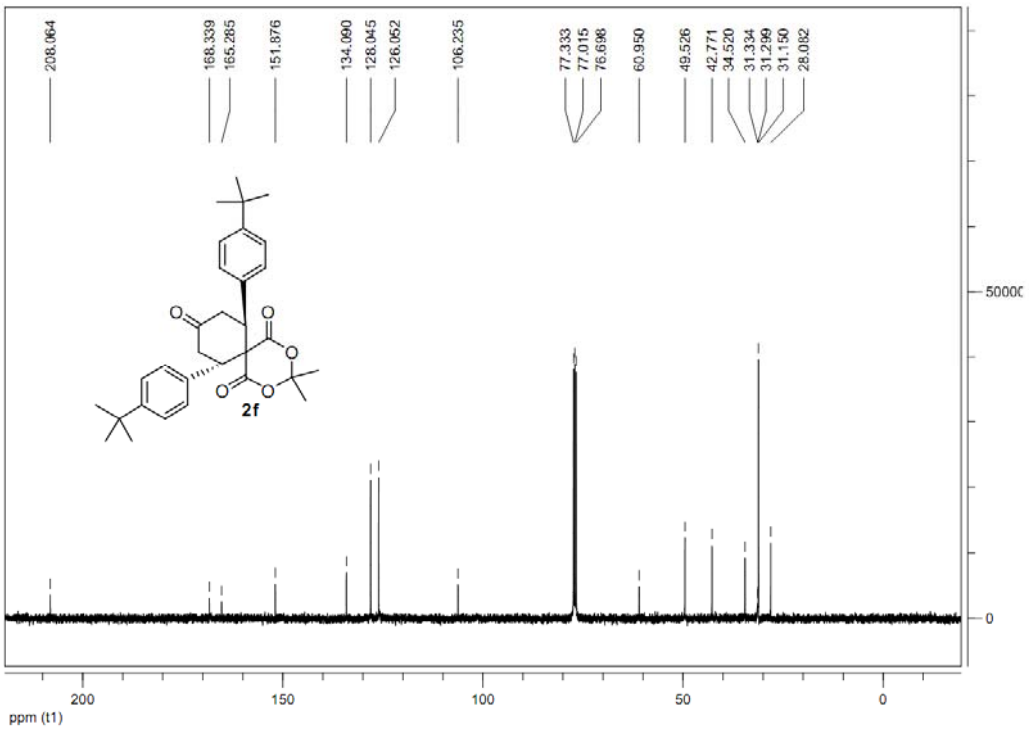

Figure 12. ^{13}C NMR spectrum ($CDCl_3$) of 2f

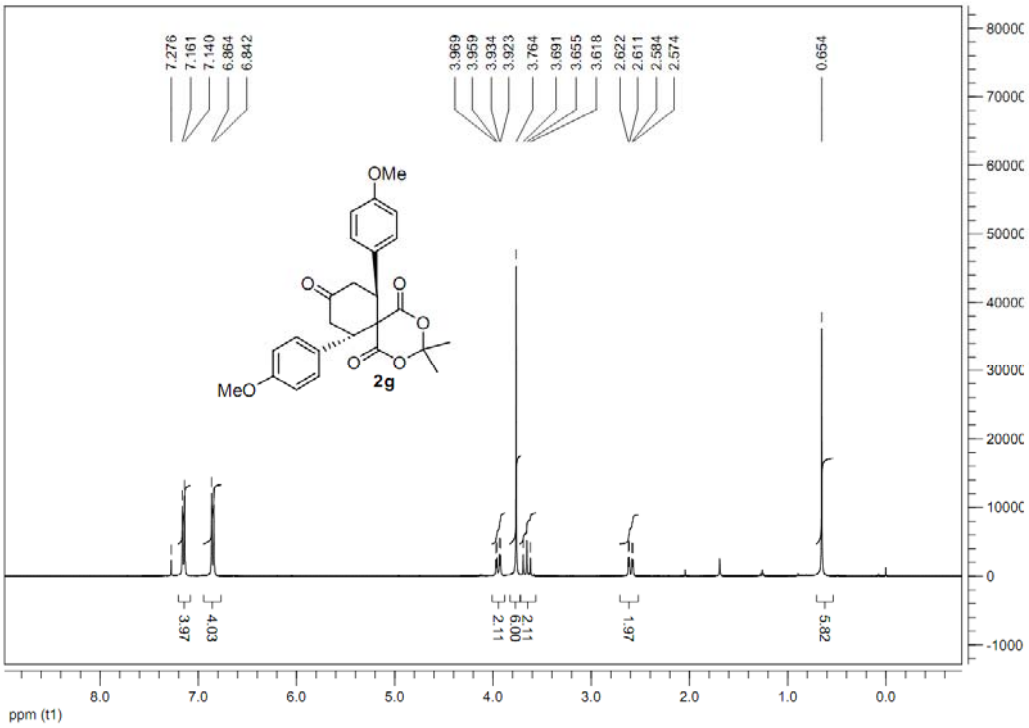

Figure 13. ^{1}H NMR spectrum ($CDCl_3$) of 2g

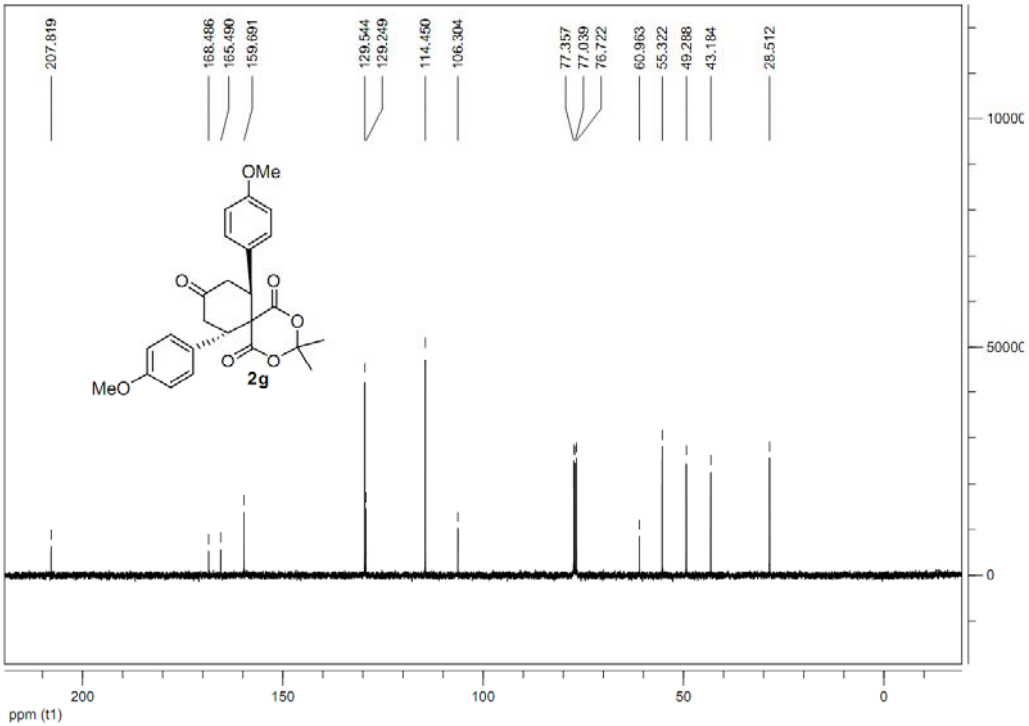

Figure 14. ^{13}C NMR spectrum ($CDCl_3$) of 2g

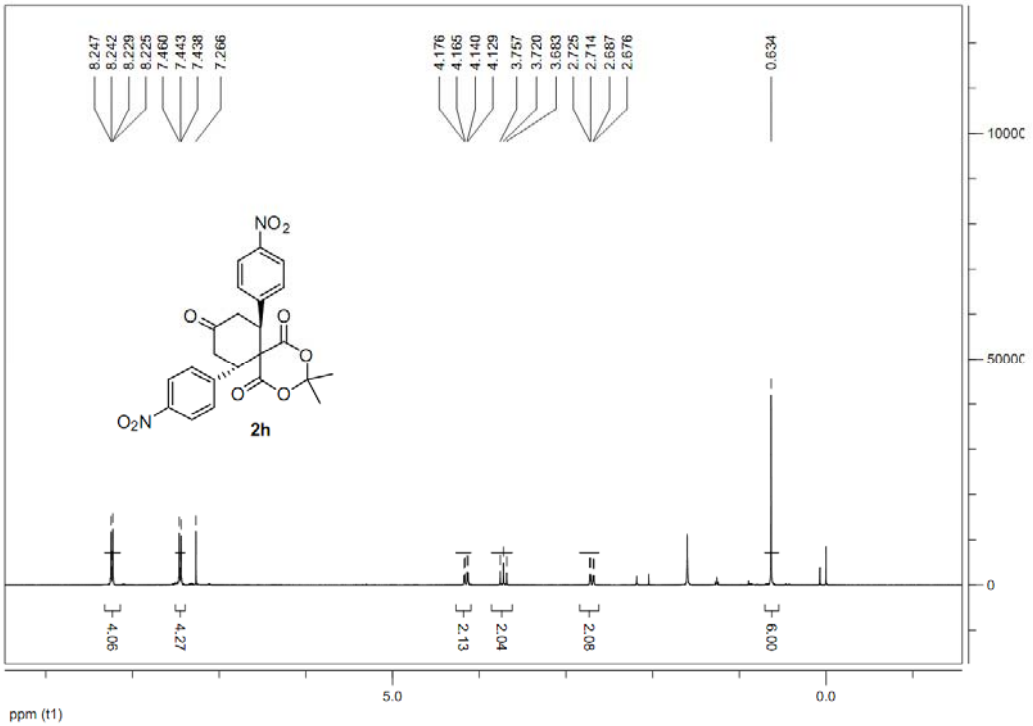

Figure 15. ^{1}H NMR spectrum ($CDCl_3$) of 2h

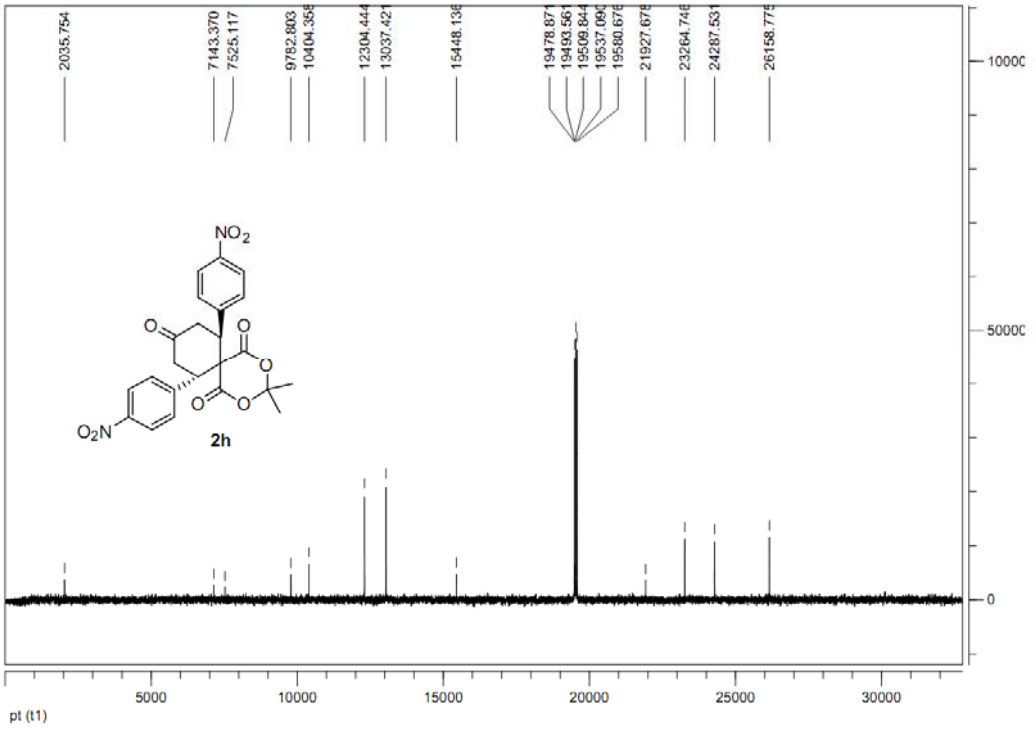

Figure 16. ^{13}C NMR spectrum ($CDCl_3$) of 2h

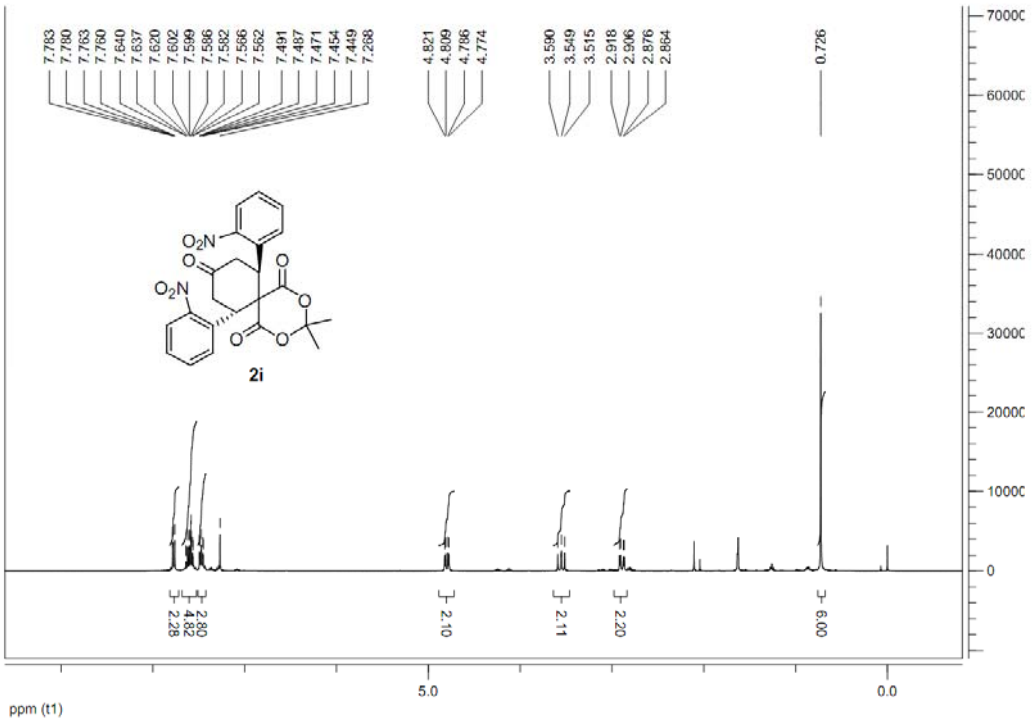

Figure 17. ^{1}H NMR spectrum ($CDCl_3$) of 2i

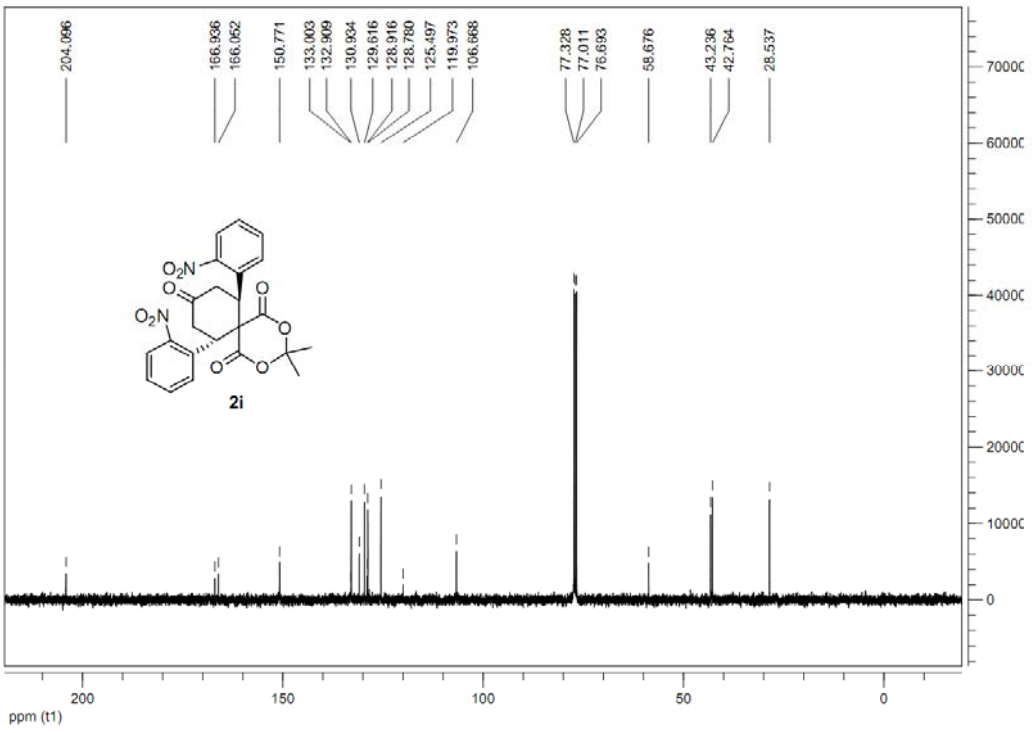

Figure 18. ^{13}C NMR spectrum ($CDCl_3$) of 2i

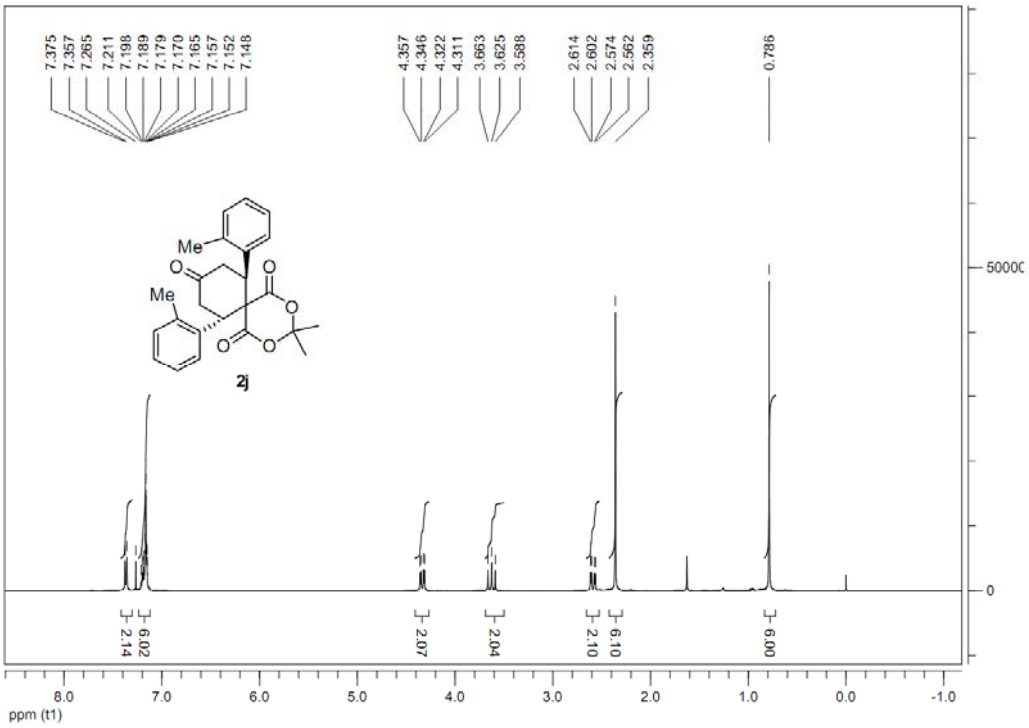

Figure 19. ^{1}H NMR spectrum ($CDCl_3$) of 2j

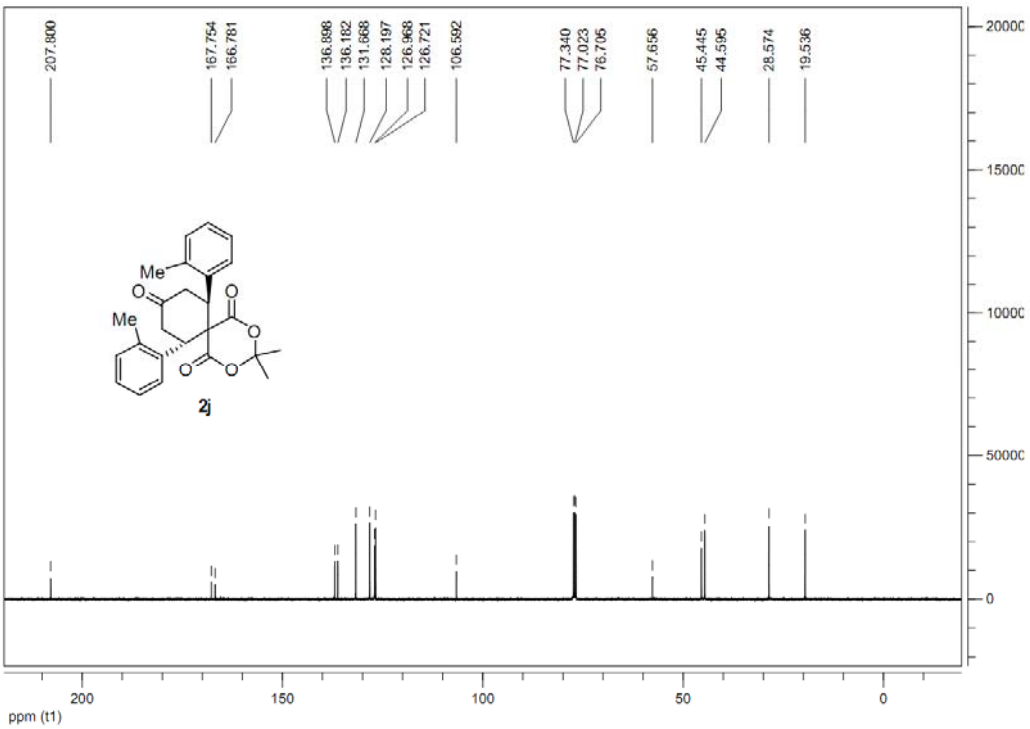

Figure 20. ^{13}C NMR spectrum ($CDCl_3$) of 2j

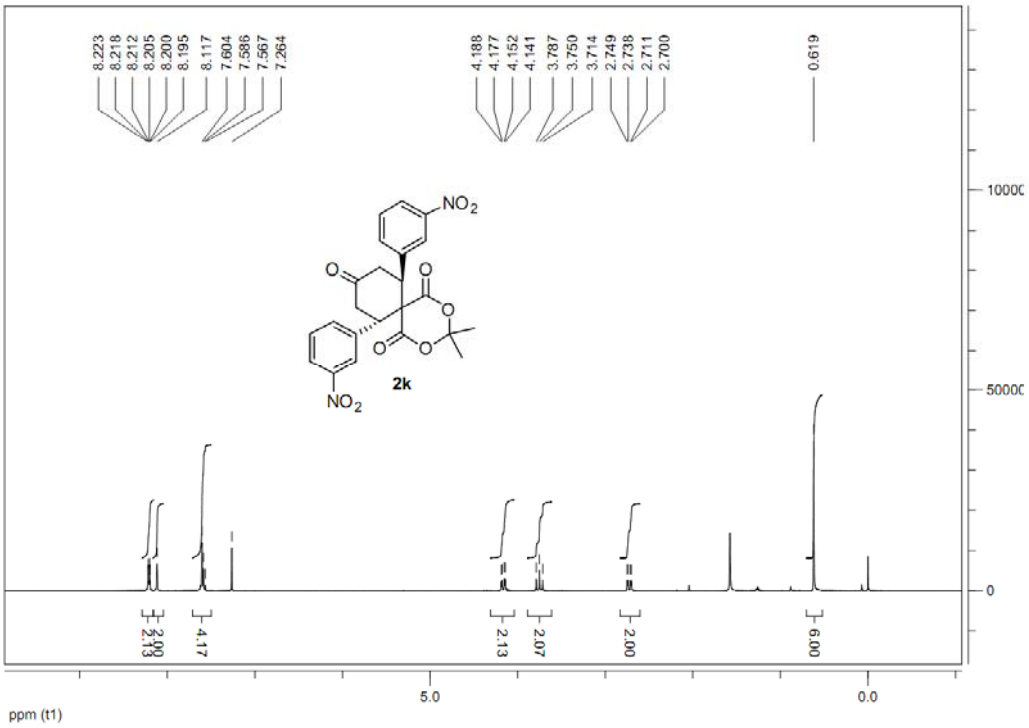

Figure 21. ^{1}H NMR spectrum ($CDCl_3$) of 2k

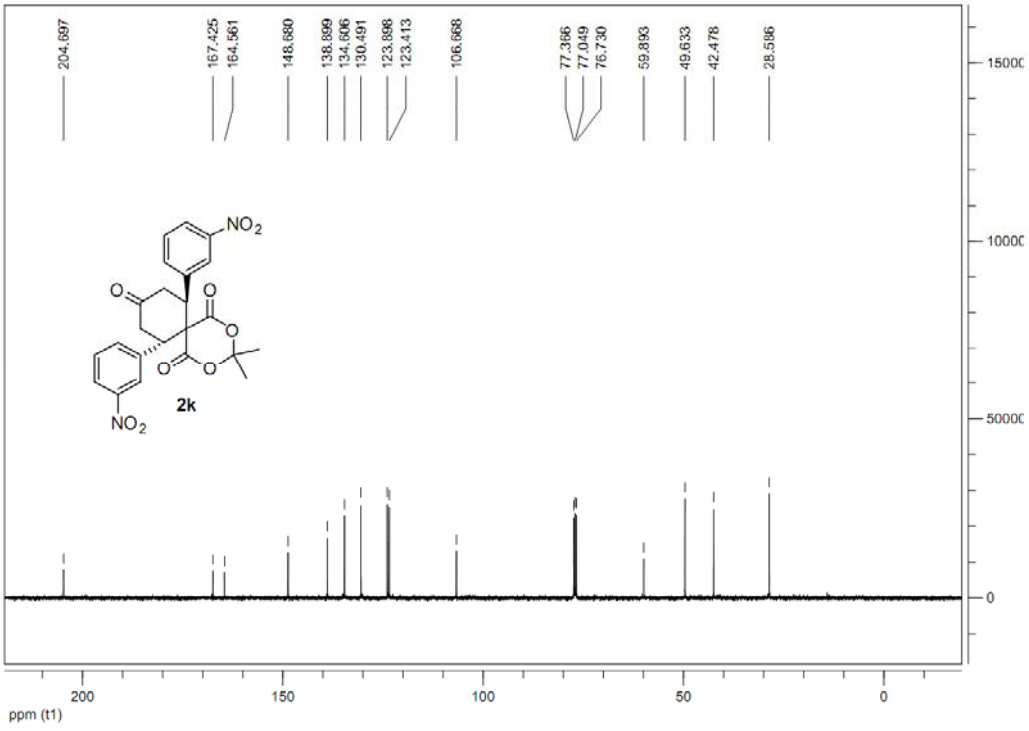

Figure 22. ^{13}C NMR spectrum ($CDCl_3$) of 2k

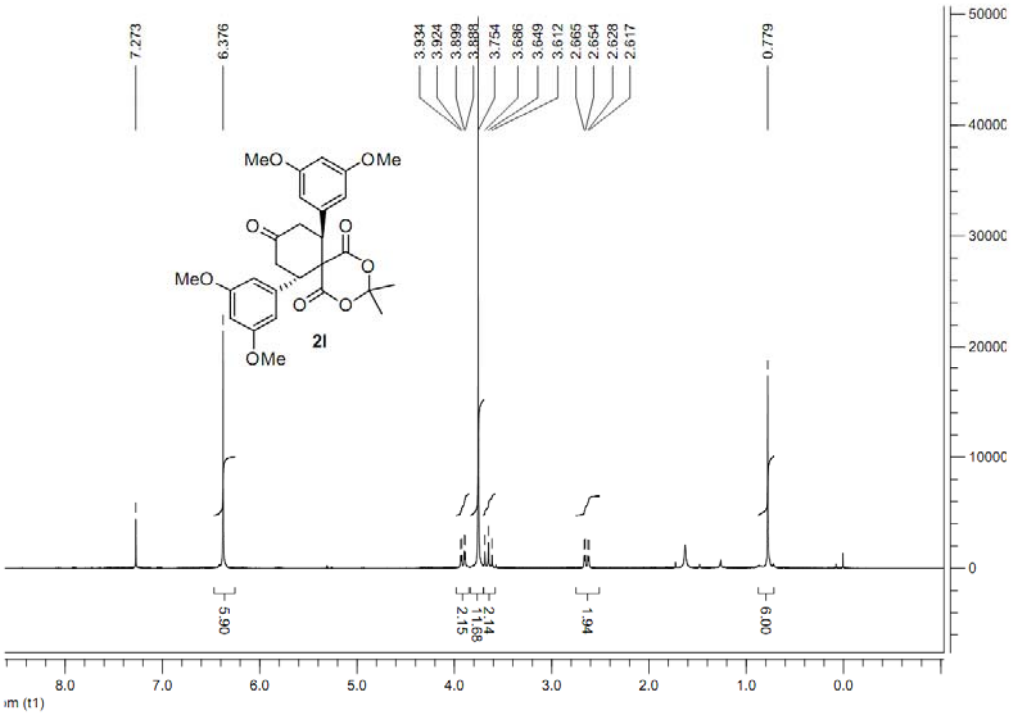

Figure 23. ^{1}H NMR spectrum ($CDCl_3$) of 2l

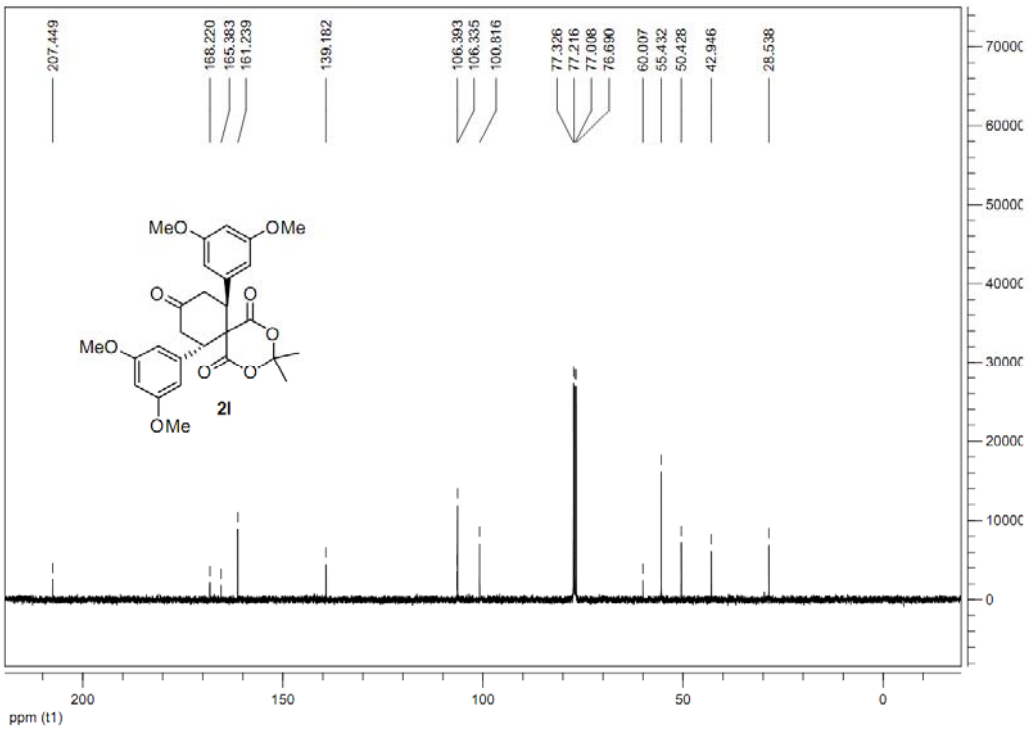

Figure 24. ^{13}C NMR spectrum ($CDCl_3$) of 2l

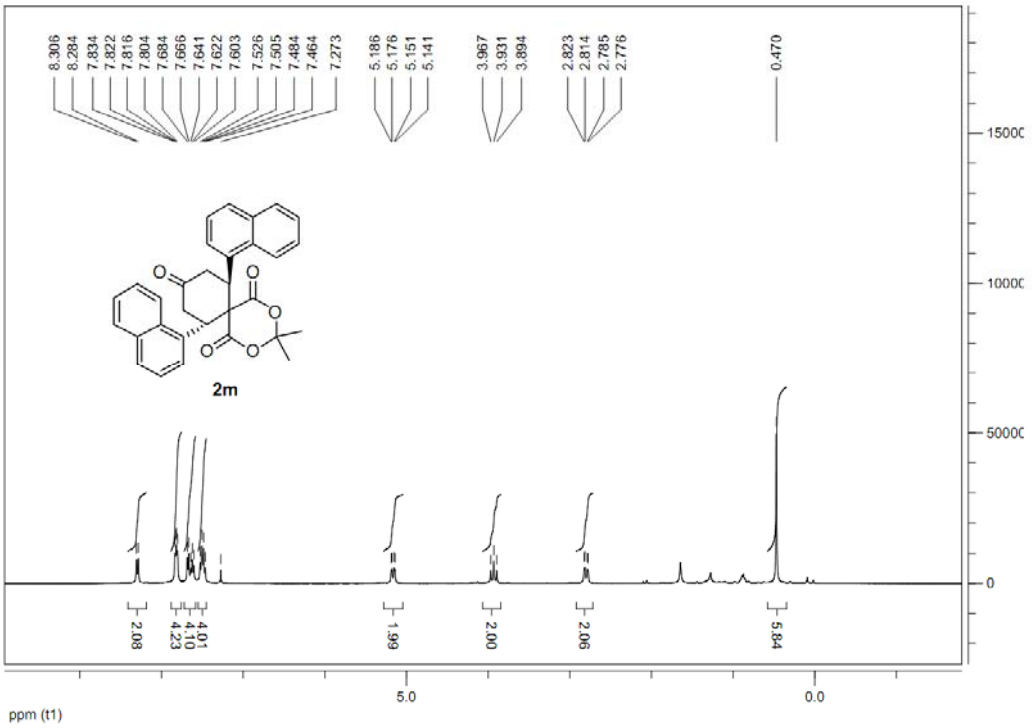

Figure 25. ^{1}H NMR spectrum ($CDCl_3$) of 2m

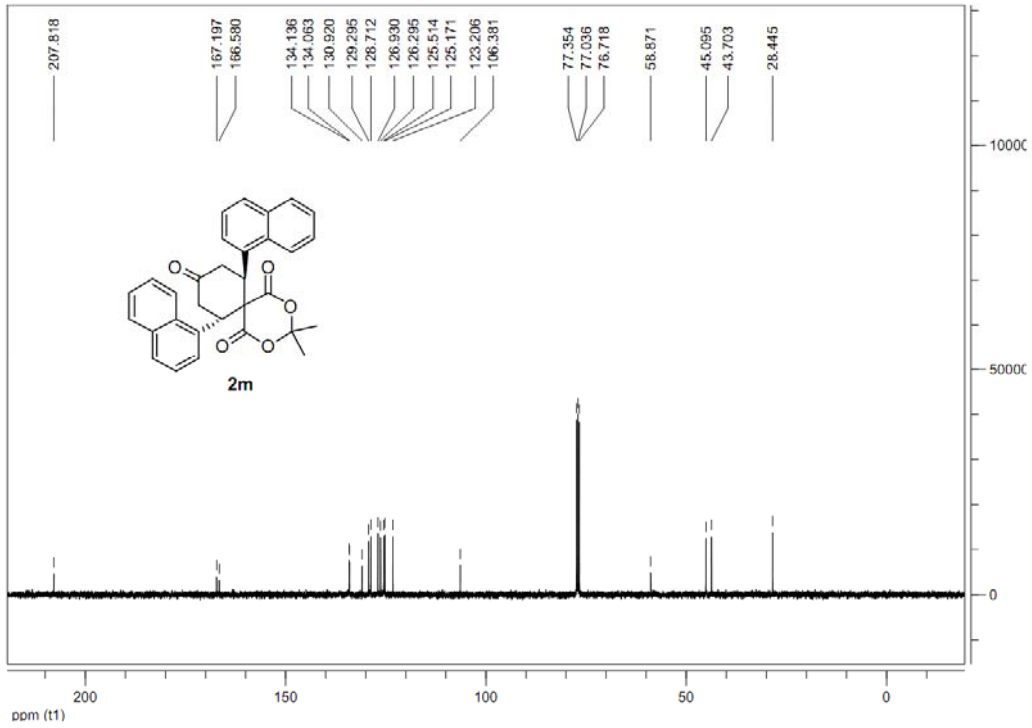

Figure 26. ^{13}C NMR spectrum ($CDCl_3$) of 2m

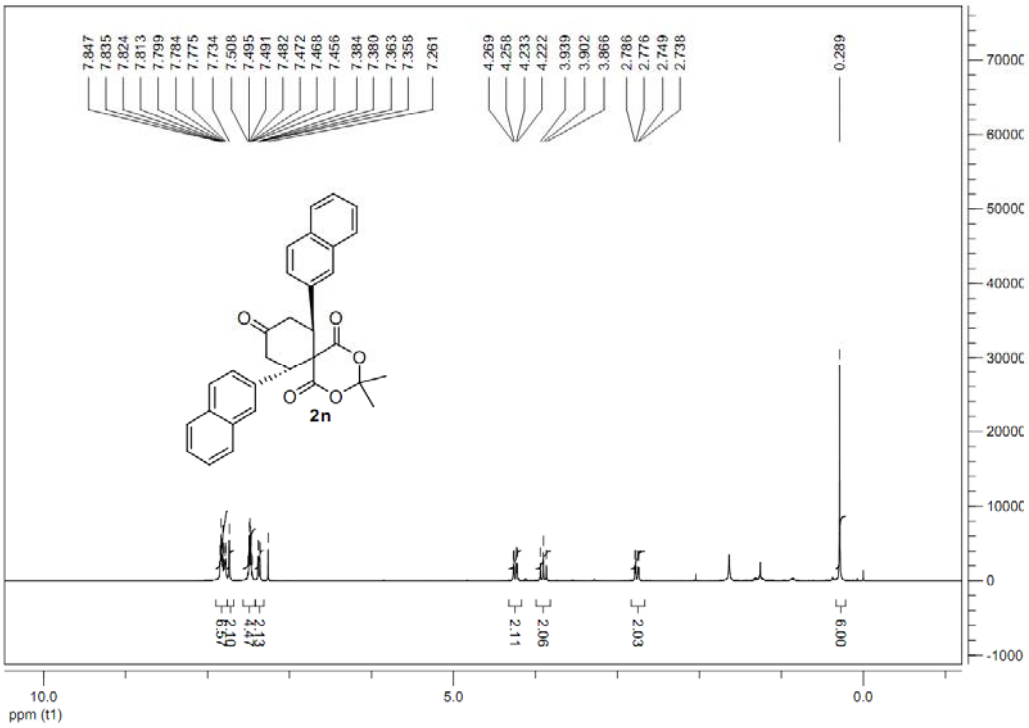

Figure 27. ^{1}H NMR spectrum ($CDCl_3$) of 2n

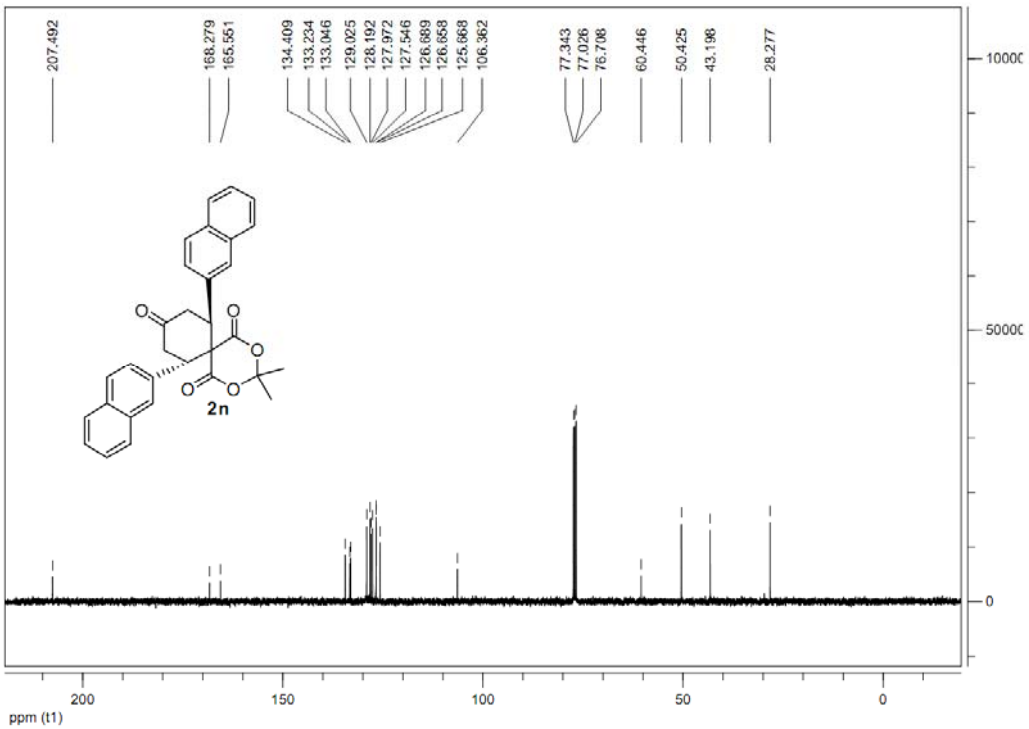

Figure 28. ^{13}C NMR spectrum ($CDCl_3$) of 2n

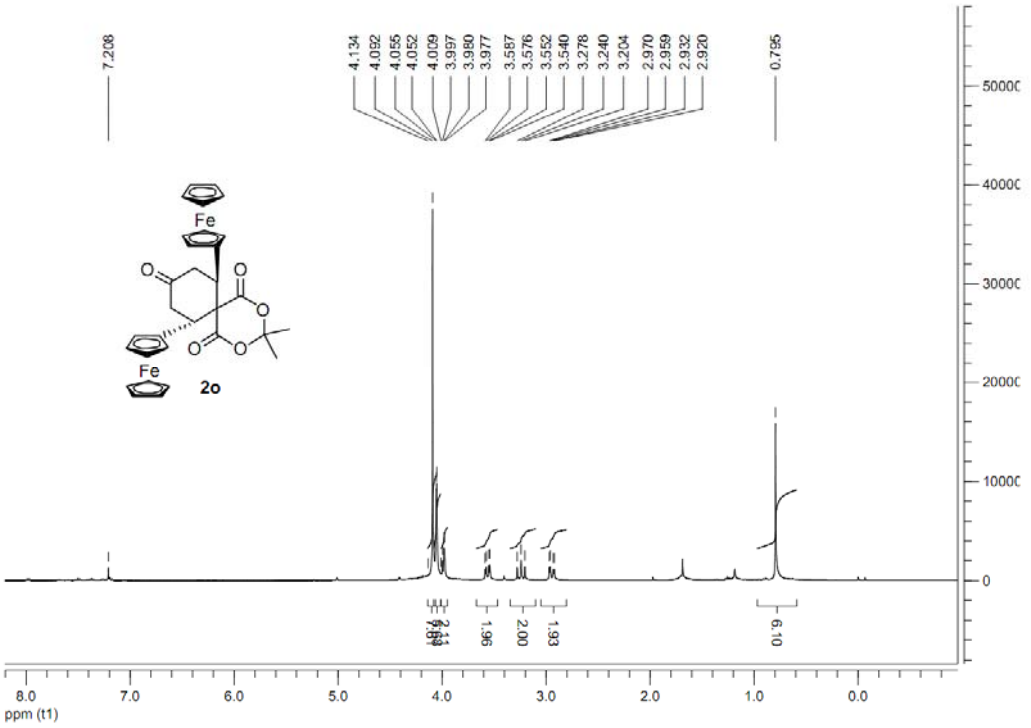

Figure 29. ^{1}H NMR spectrum ($CDCl_3$) of 2o

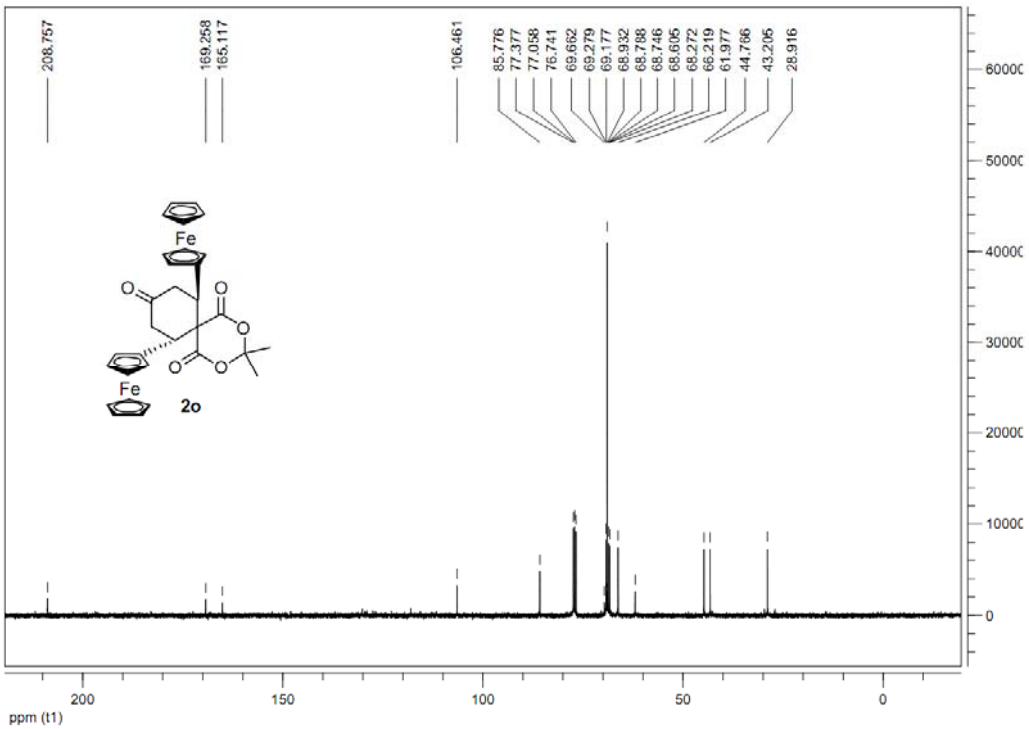

Figure 30. ^{13}C NMR spectrum ($CDCl_3$) of 2o

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