Electronic supporting information

Reactions of permethyltitanocene tucked-in derivatives with carbon dioxide

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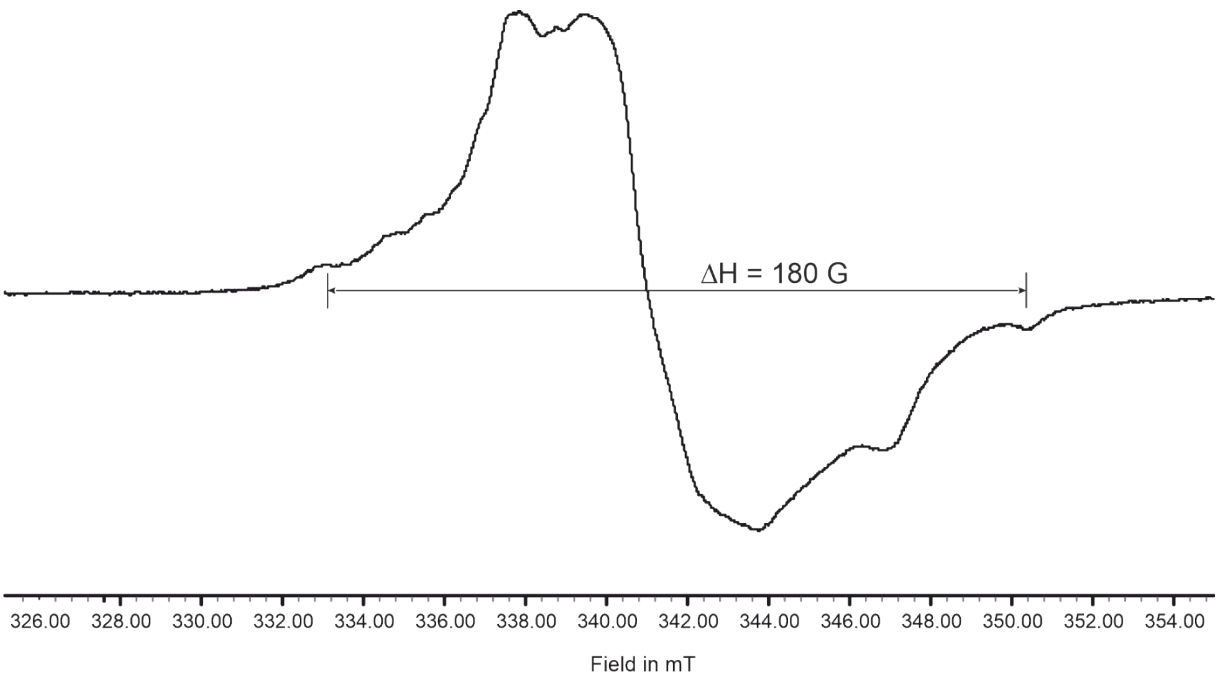
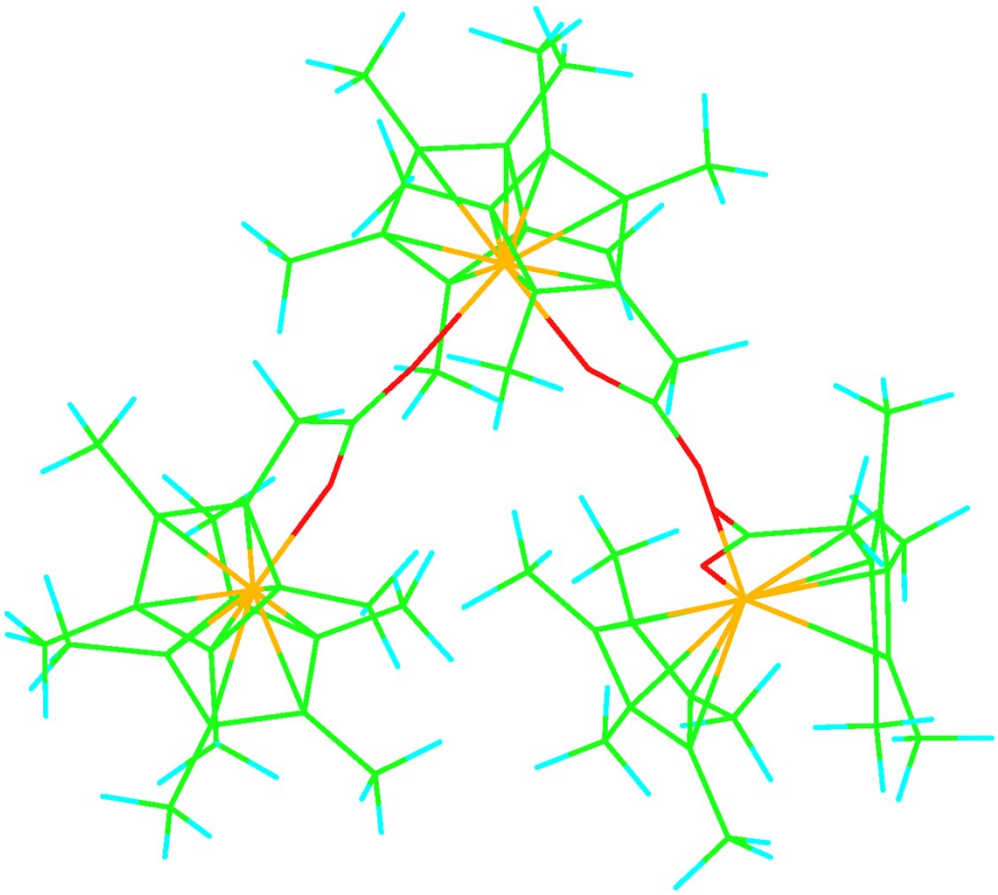
Content

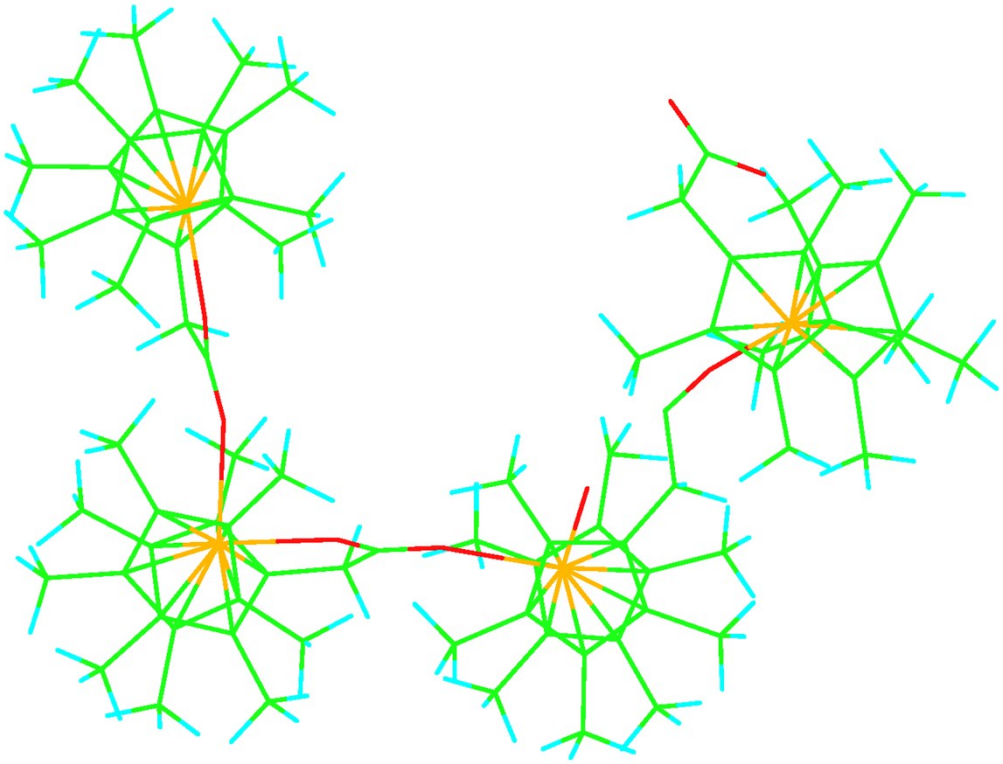
ESI Fig. 1. EPR spectrum of $[\mathbf{3}]_n$ powder at −160 °C.



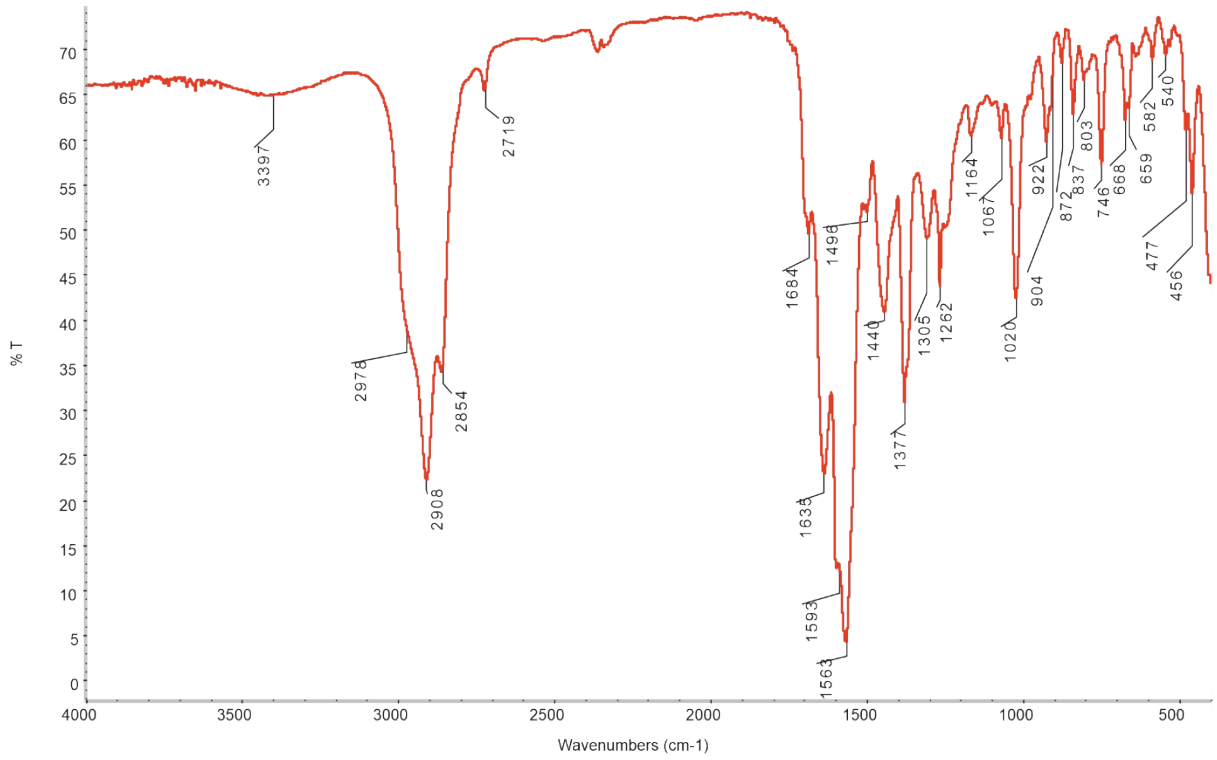
ESI Fig. 2. Computed optimized structures of trimer [**3**]$_3$.



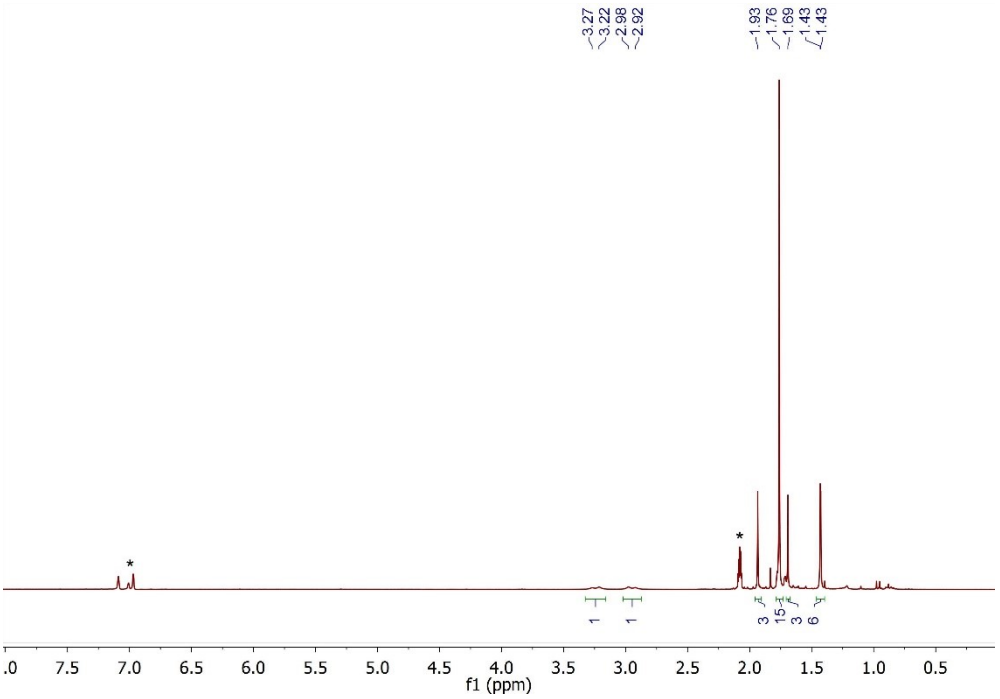
ESI Fig. 3. Computed optimized structures of tetramer $[\mathbf{3}]_4$.



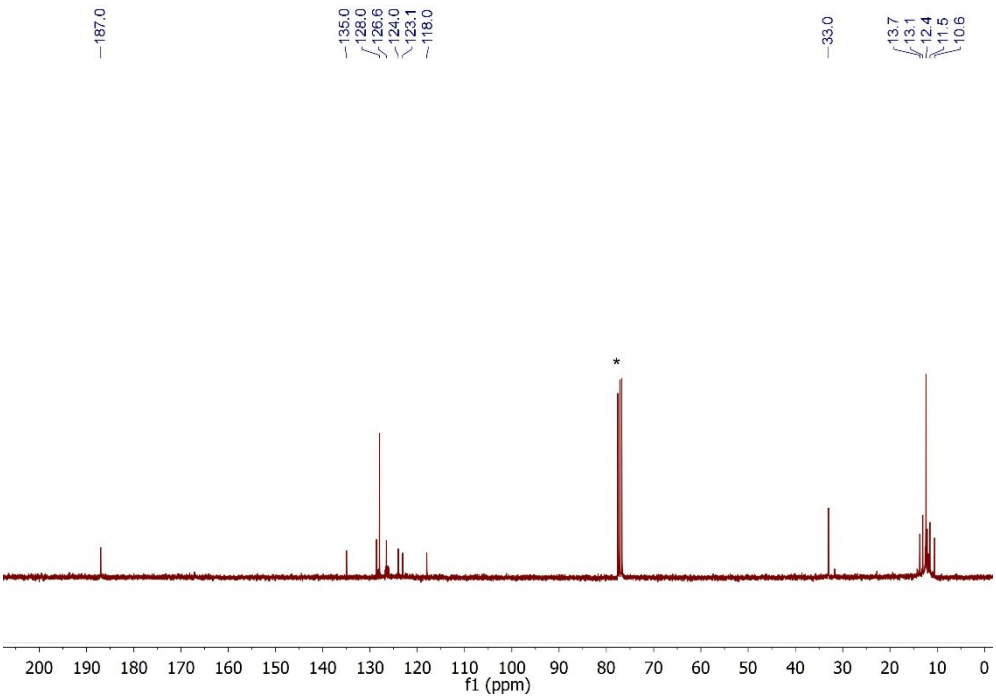
ESI Fig. 4. IR (KBr) spectrum of **3**.



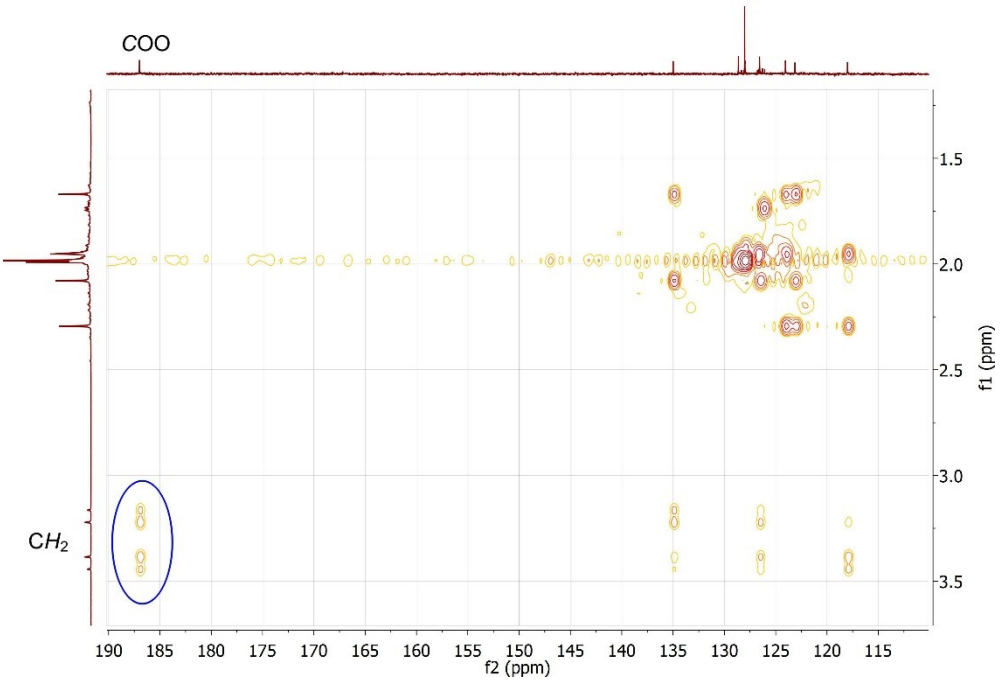
ESI Fig.5. ^{1}H NMR spectrum of **4** in toluene-d_8. (*) denote residual proton signals of the solvent.



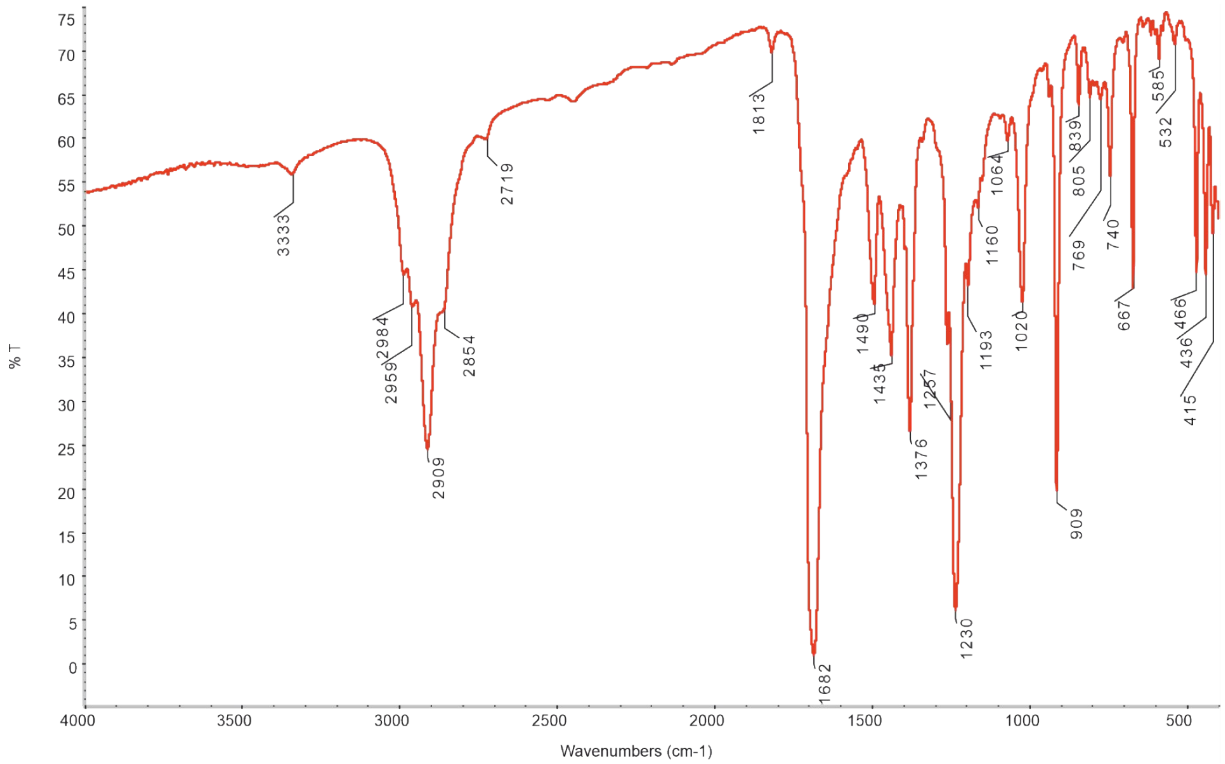
ESI Fig. 6. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$. (*) denotes the solvent signal.



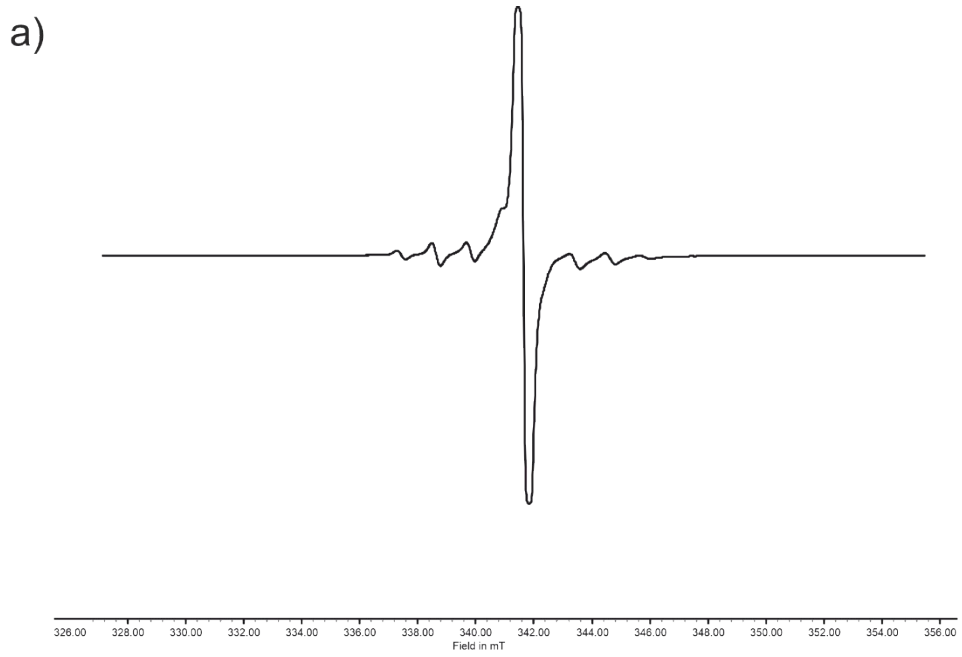
ESI Fig. 7. gHMBC spectrum of **4** in $CDCl_3$. Cross-peaks showing the interaction between methylene group and caboxylate carbon are highlighted by blue ellipse.

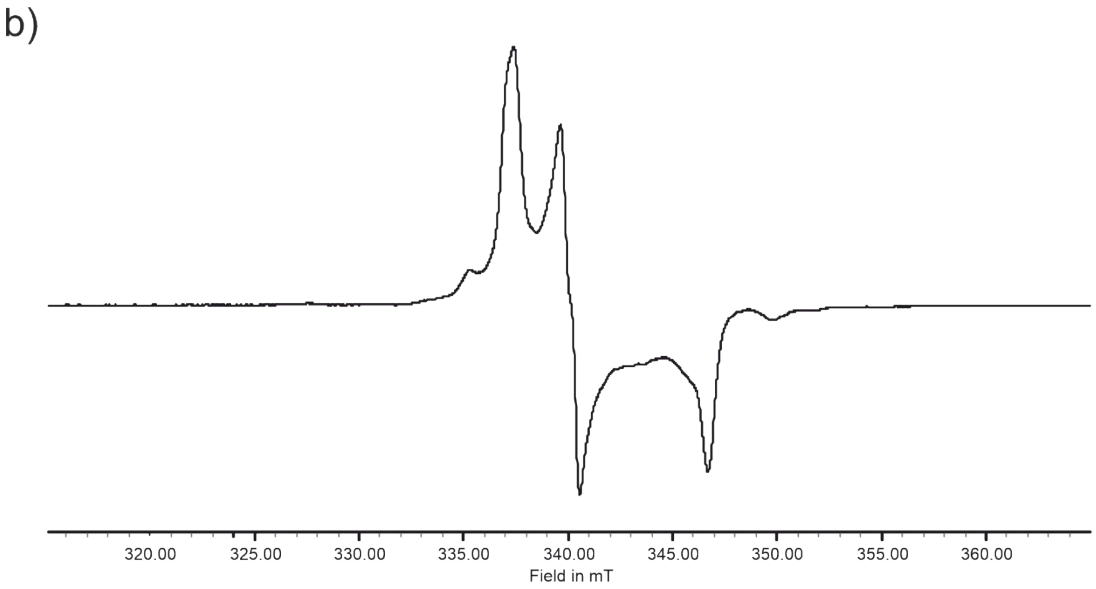


ESI Fig. 8. IR (KBr) spectrum of **4**.

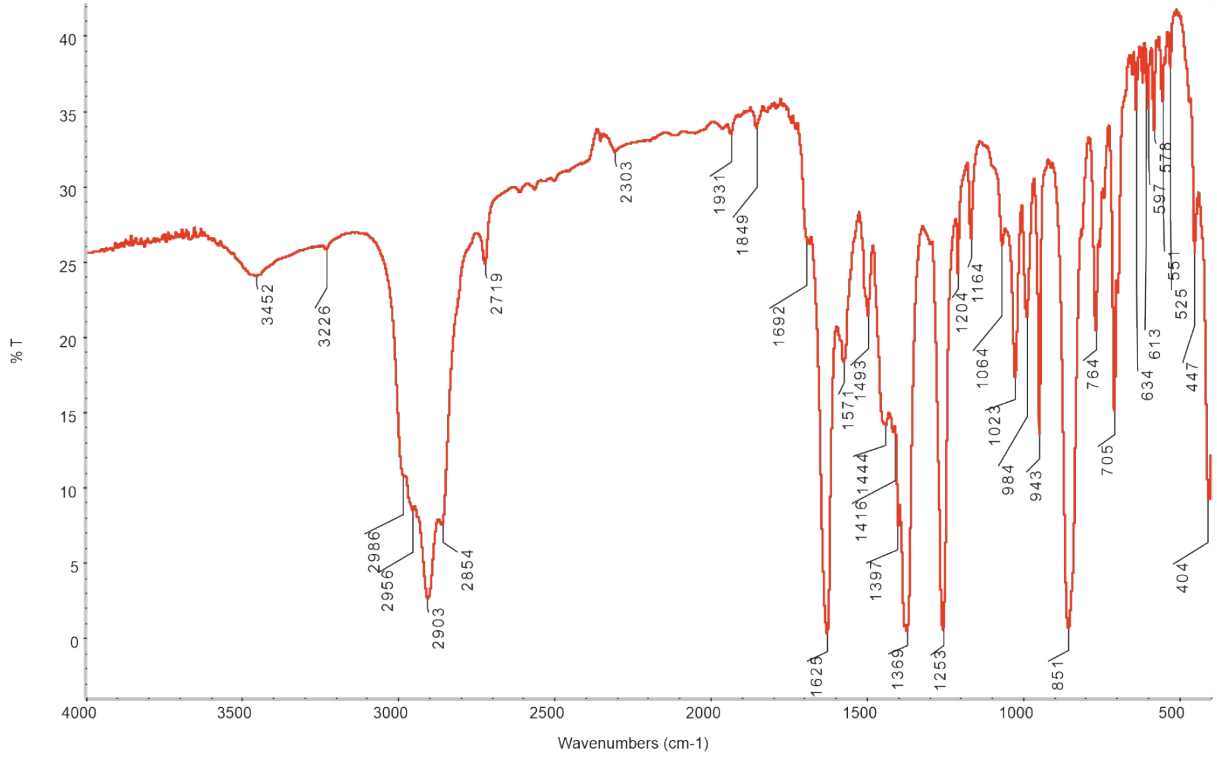


ESI Fig. 9. EPR spectrum of **5** in toluene solution at 20 °C (a) and glass at −160 °C (b).

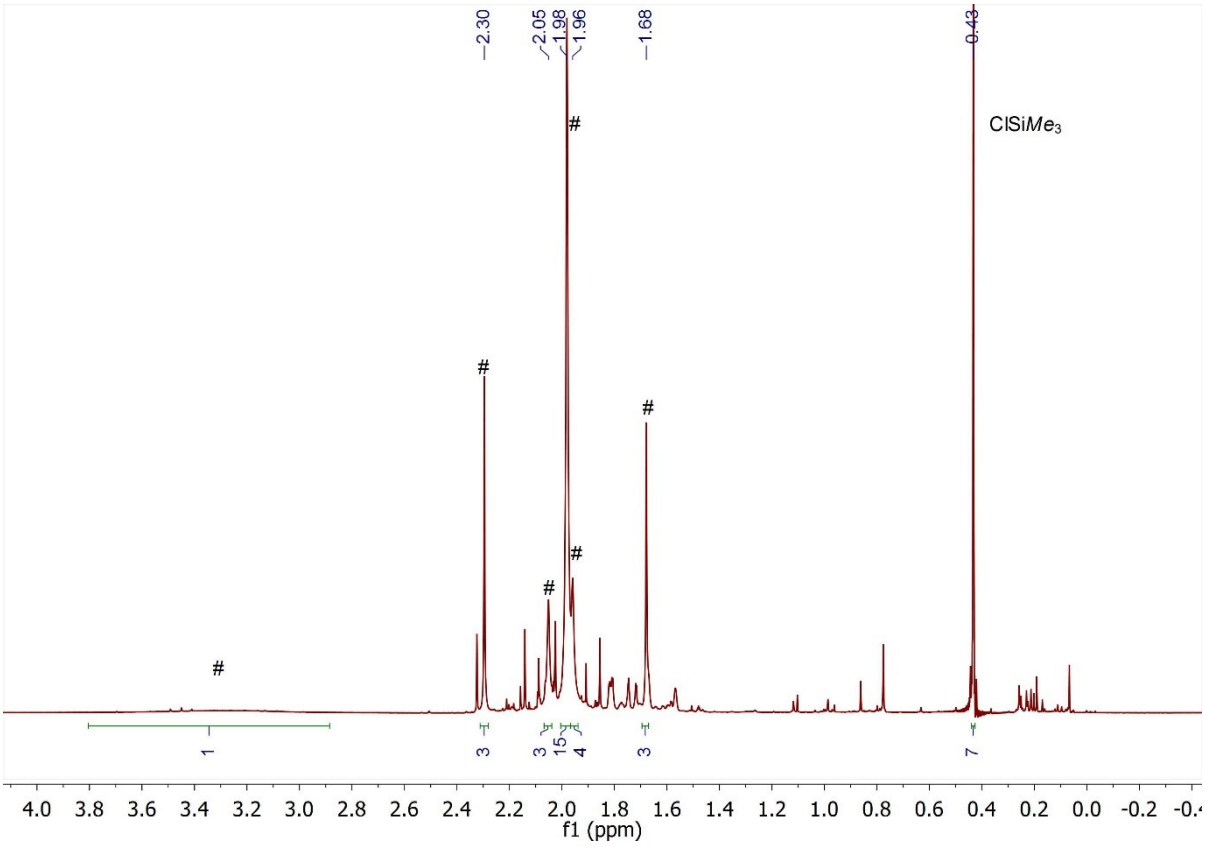




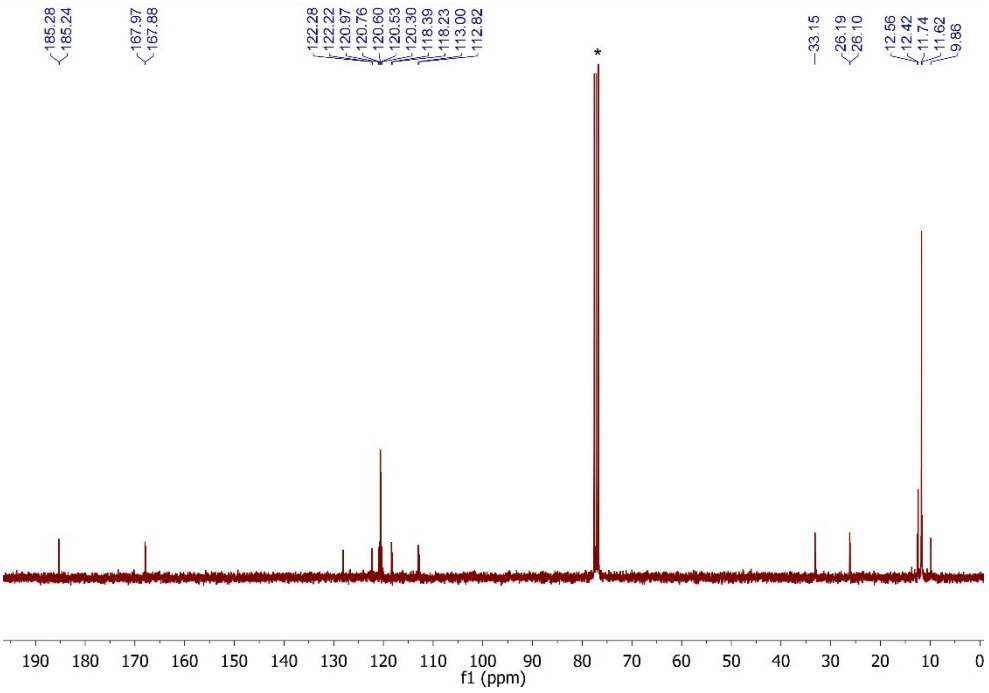
ESI Fig. 10. IR (KBr) spectrum of **5**.



ESI Fig. 11. ^{1}H NMR spectrum of products formed after dissolution of **5** in CD_2Cl_2. Signals of formed **4** are denoted (#), signal of ClSi*Me*$_3$ was detected at 0.43 ppm. The spectrum was taken in a "quantitative" mode with d1=50s.

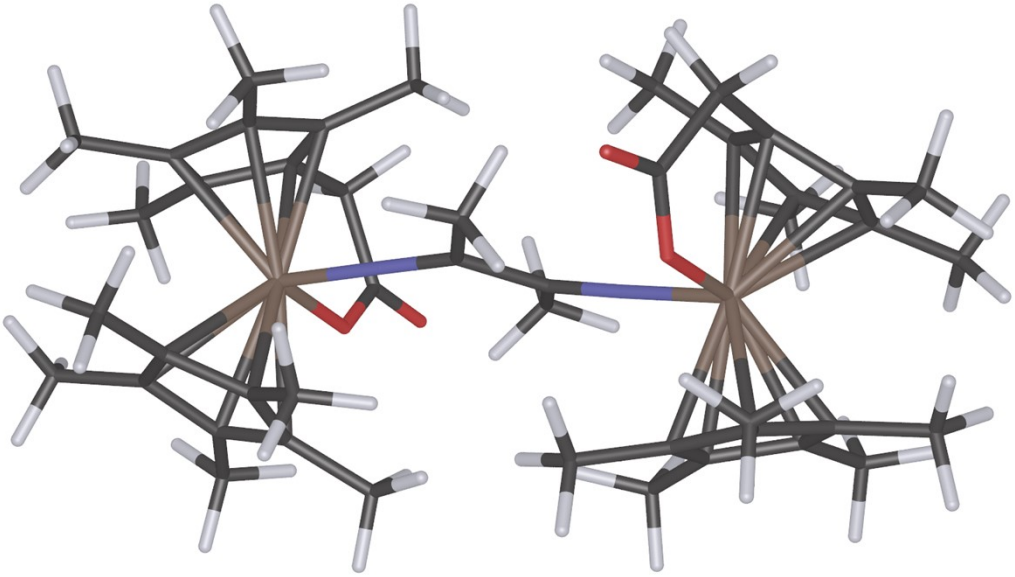


ESI Fig. 12. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

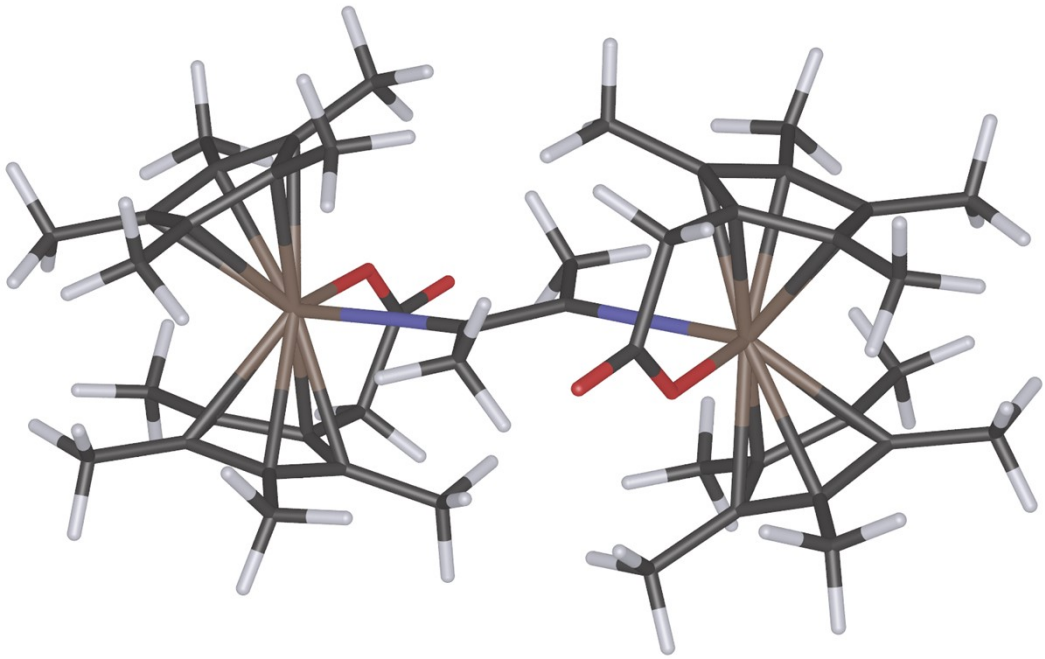


ESI Fig. 13. Computed optimized structures of **6** with C_2 (a) and C_i (b) symmetry.

(a)

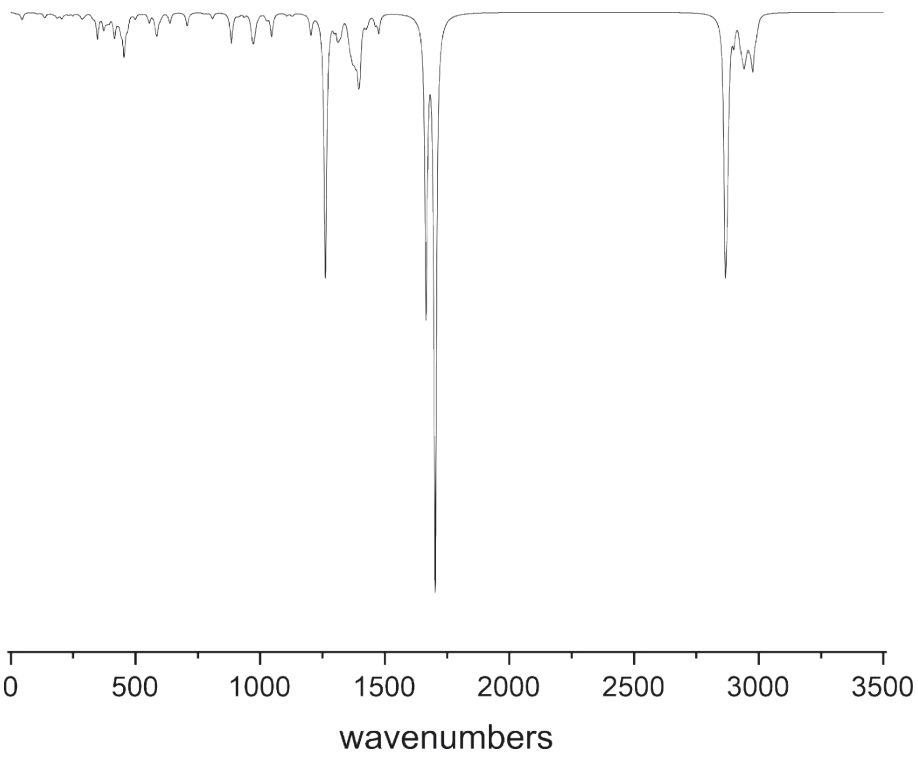


(b)

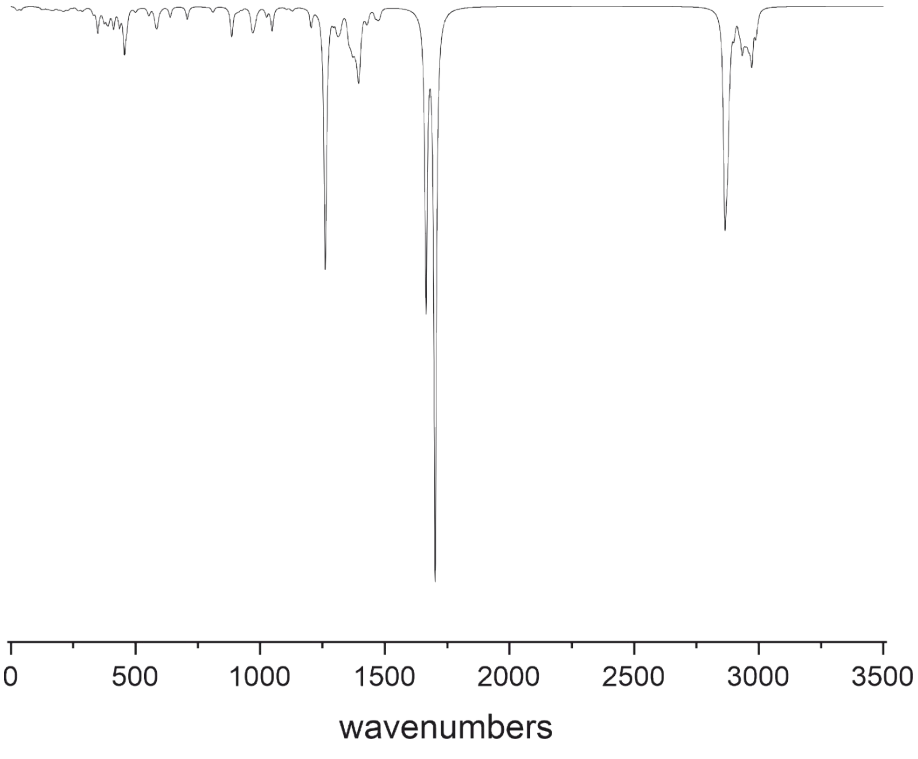


ESI Fig. 14. Computed IR spectra of **6** with C_2 (a) and C_i (b) symmetry scaled by 0.95.

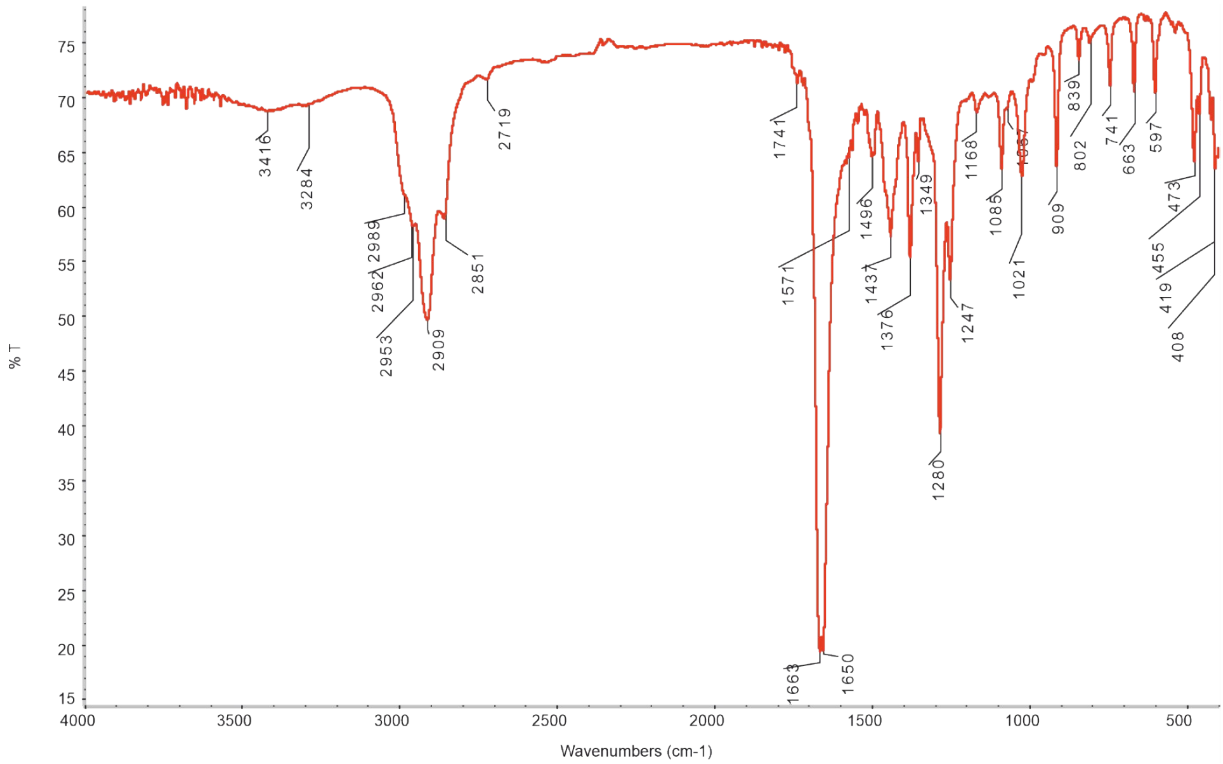
(a)



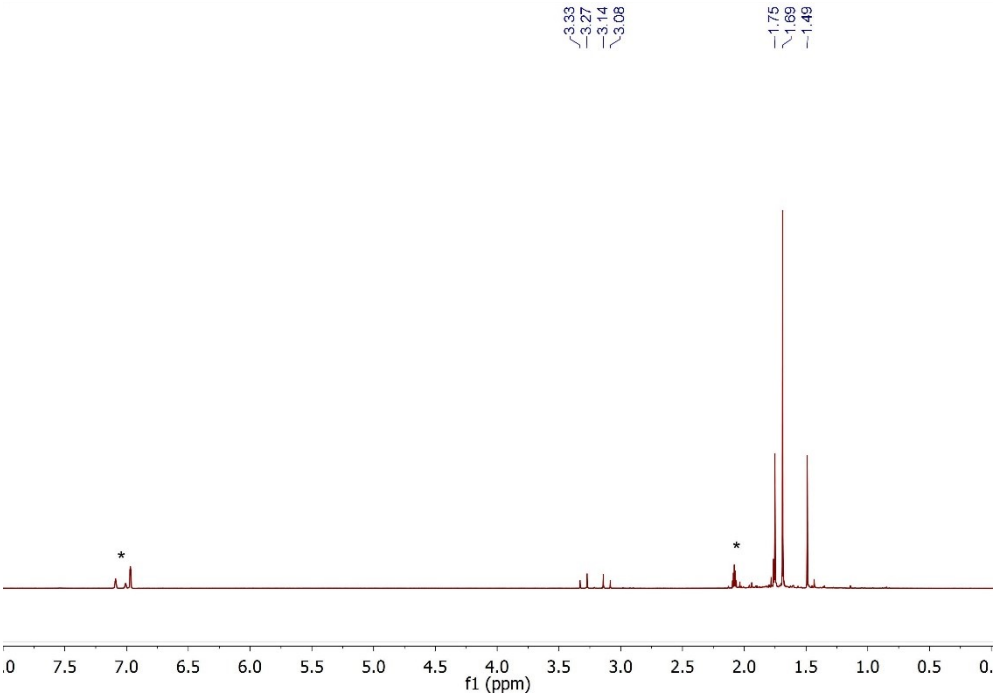
(b)



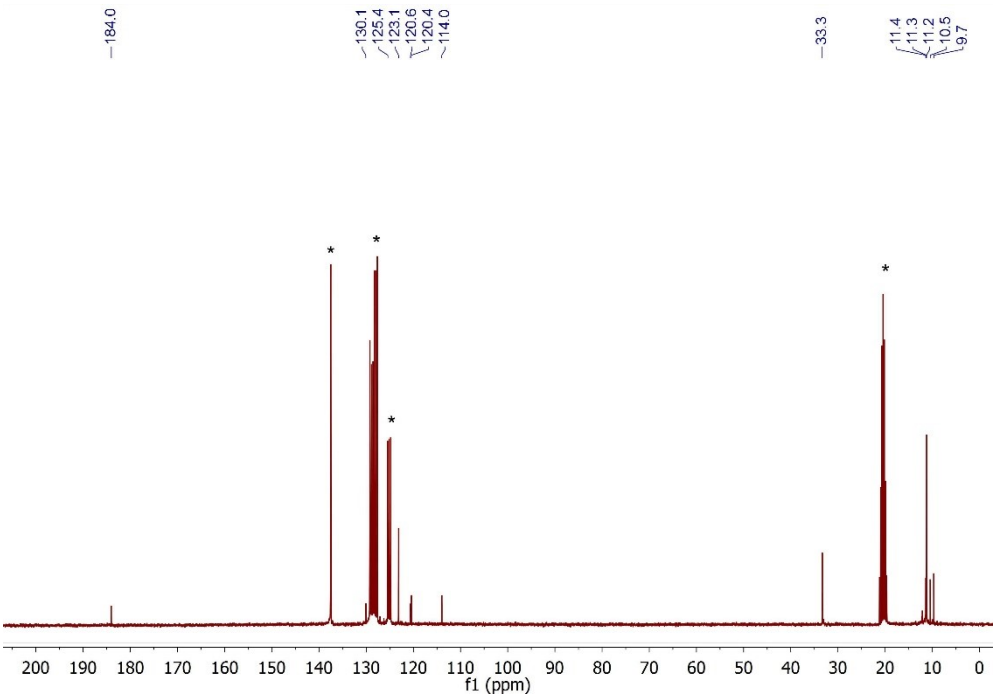
ESI Fig. 15. IR (KBr) spectrum of **6**.



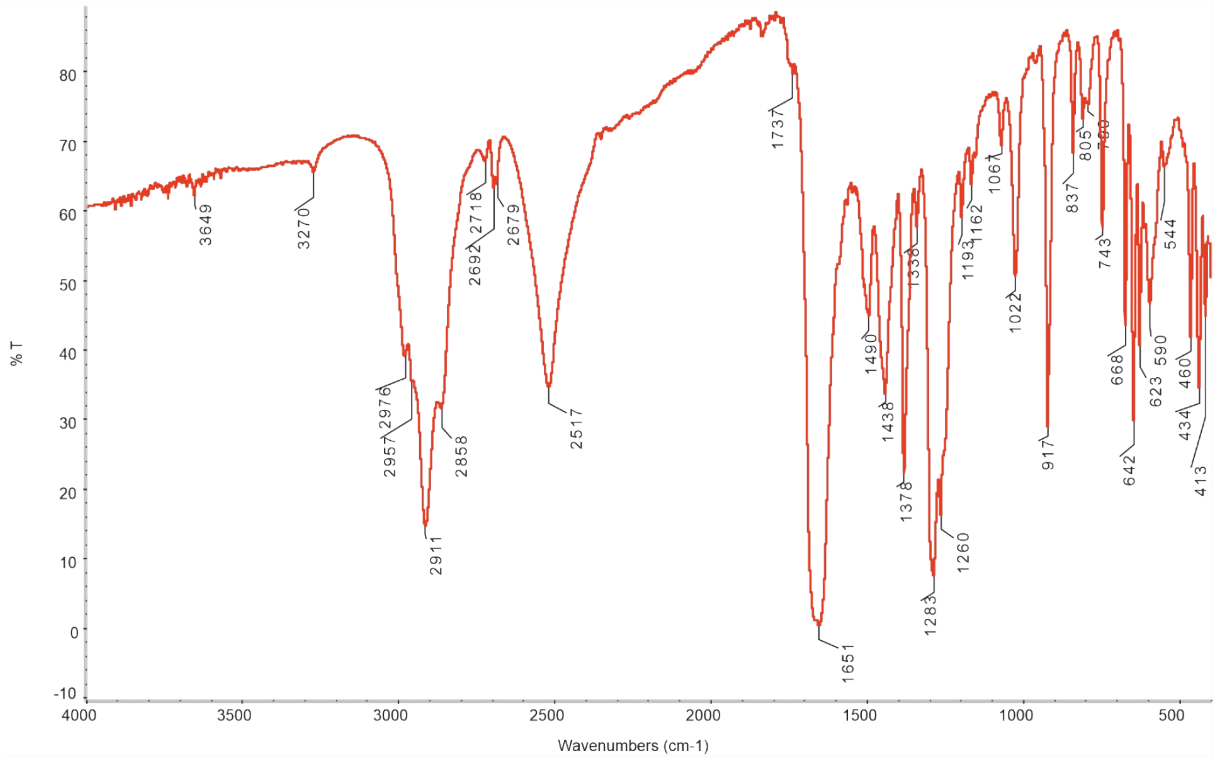
ESI Fig. 16. ^{1}H NMR spectrum of **7** toluene-d_8. (*) denote residual proton signals of the solvent.



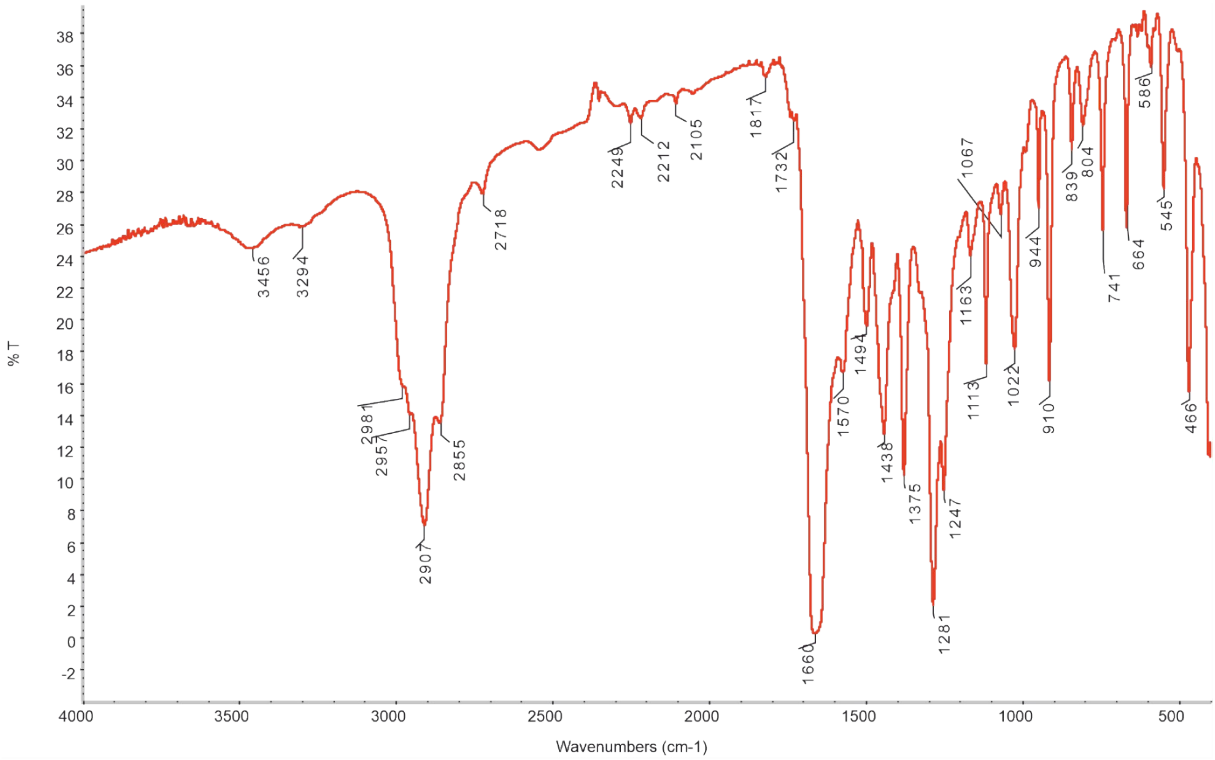
ESI Fig. 17. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in toluene-d_8. (*) denote solvent signals.



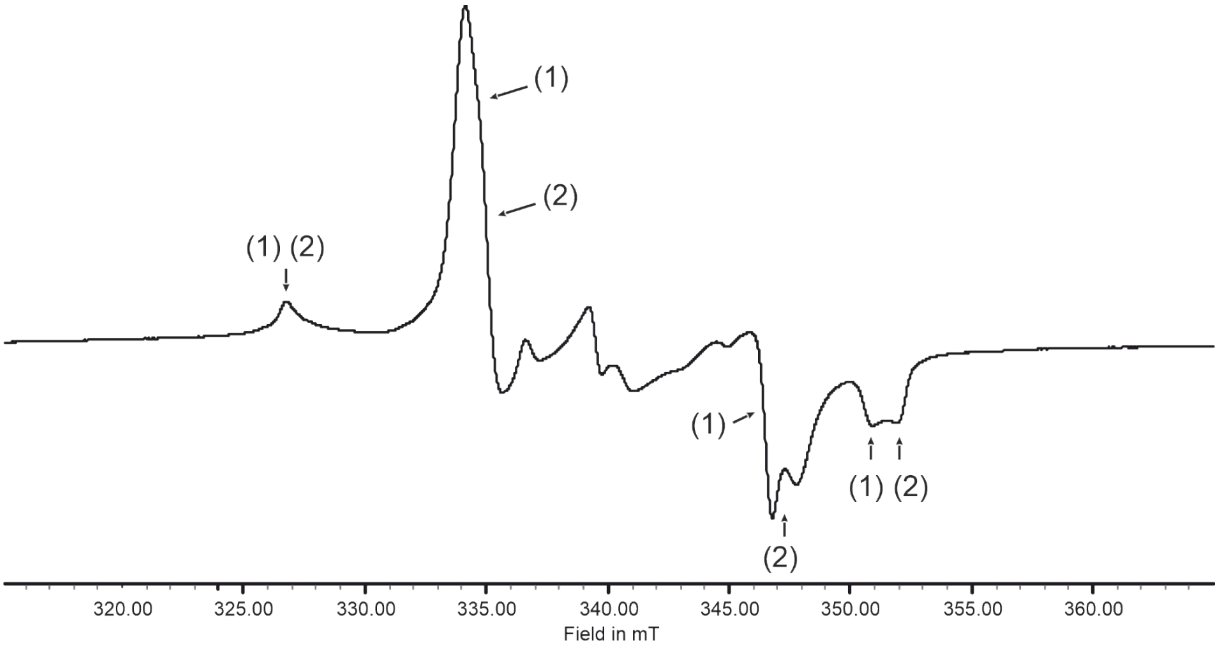
ESI Fig. 18. IR (KBr) spectrum of 7.



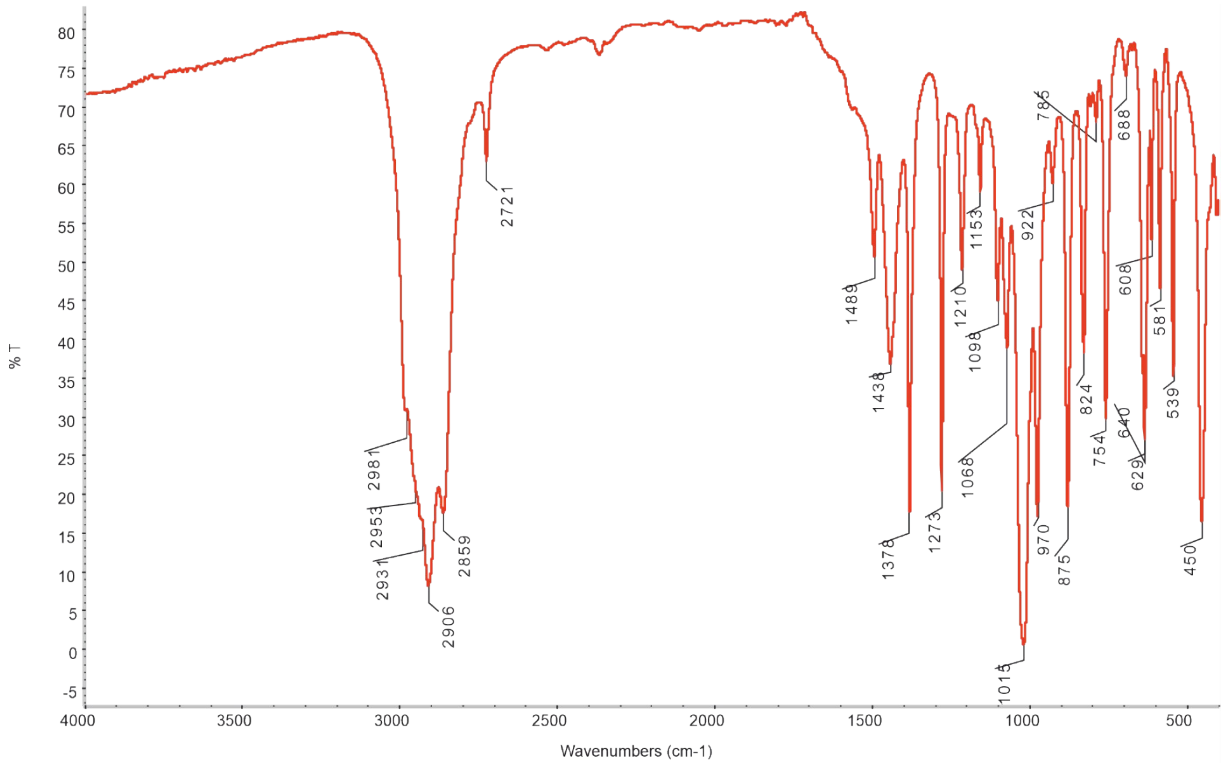
ESI Fig. 19. IR spectrum of **6a**.



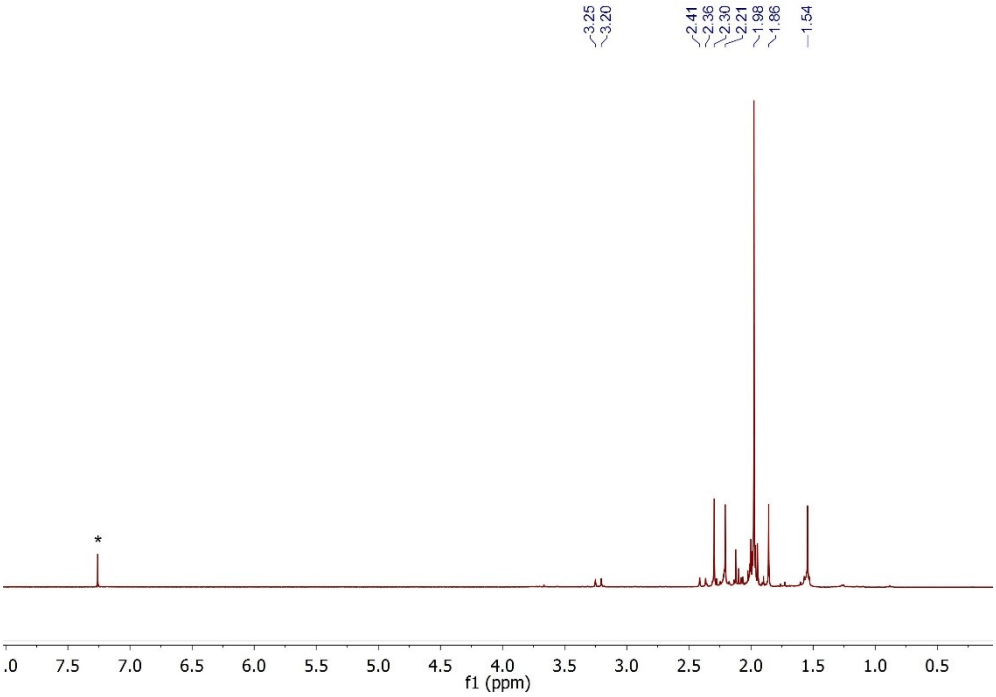
ESI Fig. 20. EPR spectrum of **8** in toluene at −160 °C. Features of axially symmetric electronic triplet state species (1) and (2) denoted by arrows. Negligible impurity in central part: $g_1 = 2.000$, $g_2 = 1.983$, $g_3 = 1.952$, $g_{av} = 1.978$ – typical parameters for Cp^*_2TiOR (R = alkyl).



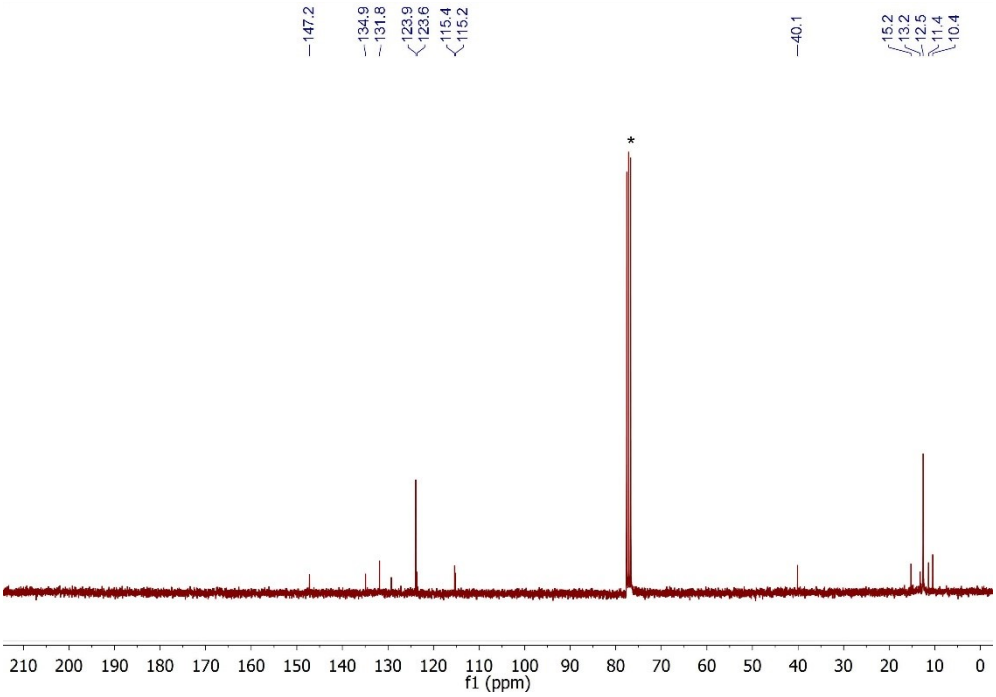
ESI Fig. 21. IR (KBr) spectrum of **8**.



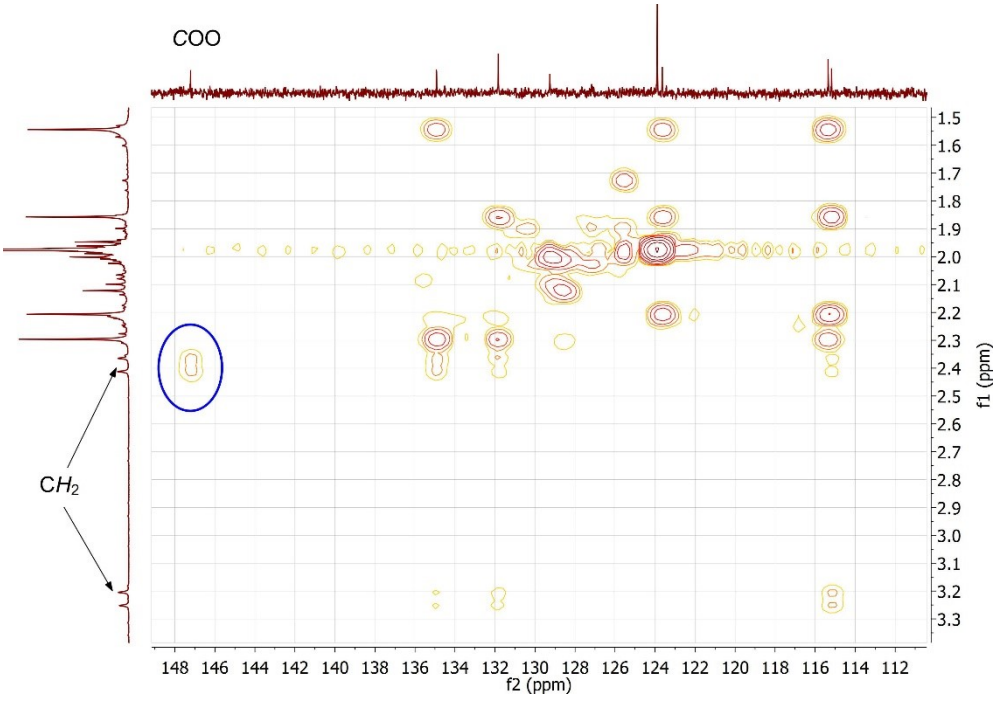
ESI Fig. 22. ^{1}H NMR spectrum of **9** in $CDCl_3$. (*) denotes residual proton signal of the solvent.



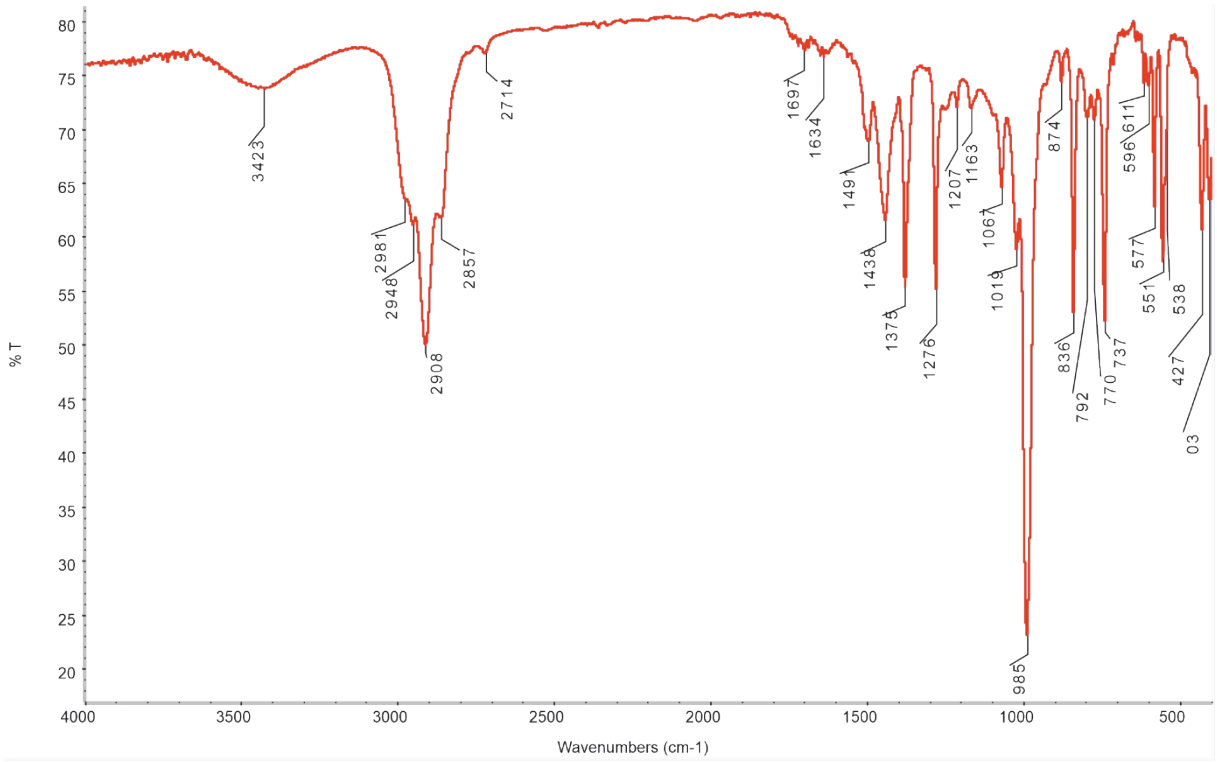
ESI Fig. 23. $^{13}C\{^{1}H\}$ NMR spectrum of **9** in $CDCl_3$. (*) denotes a solvent signal.



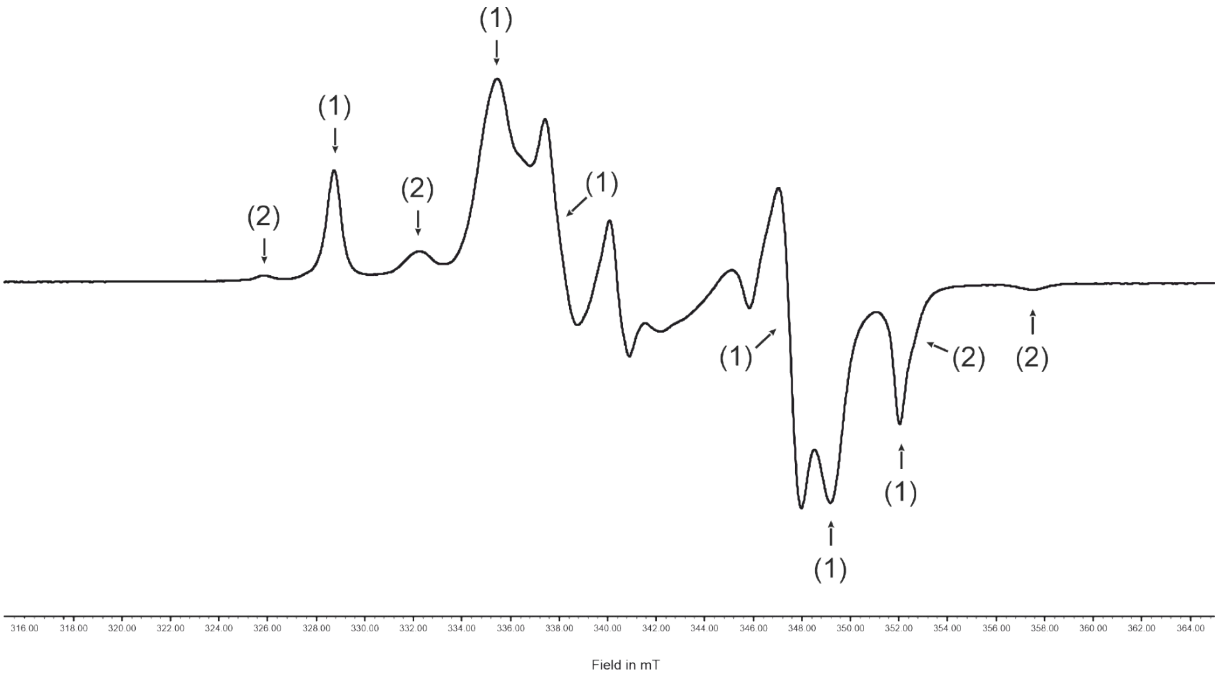
ESI Fig. 24. gHMBC spectrum of **9** in $CDCl_3$. Cross-peak showing the interaction between a proton of methylene group and bridging diolate carbon is highlighted by blue ellipse.



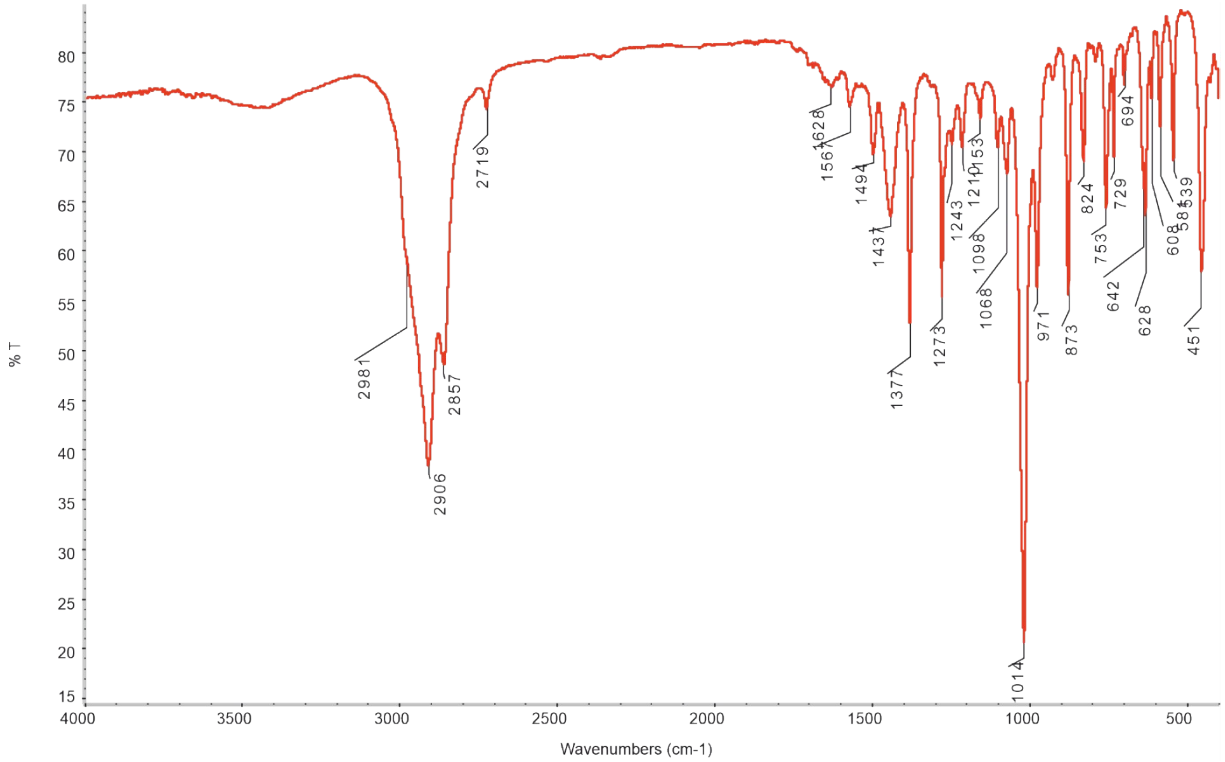
ESI Fig. 25. IR (KBr) spectrum of **9**.



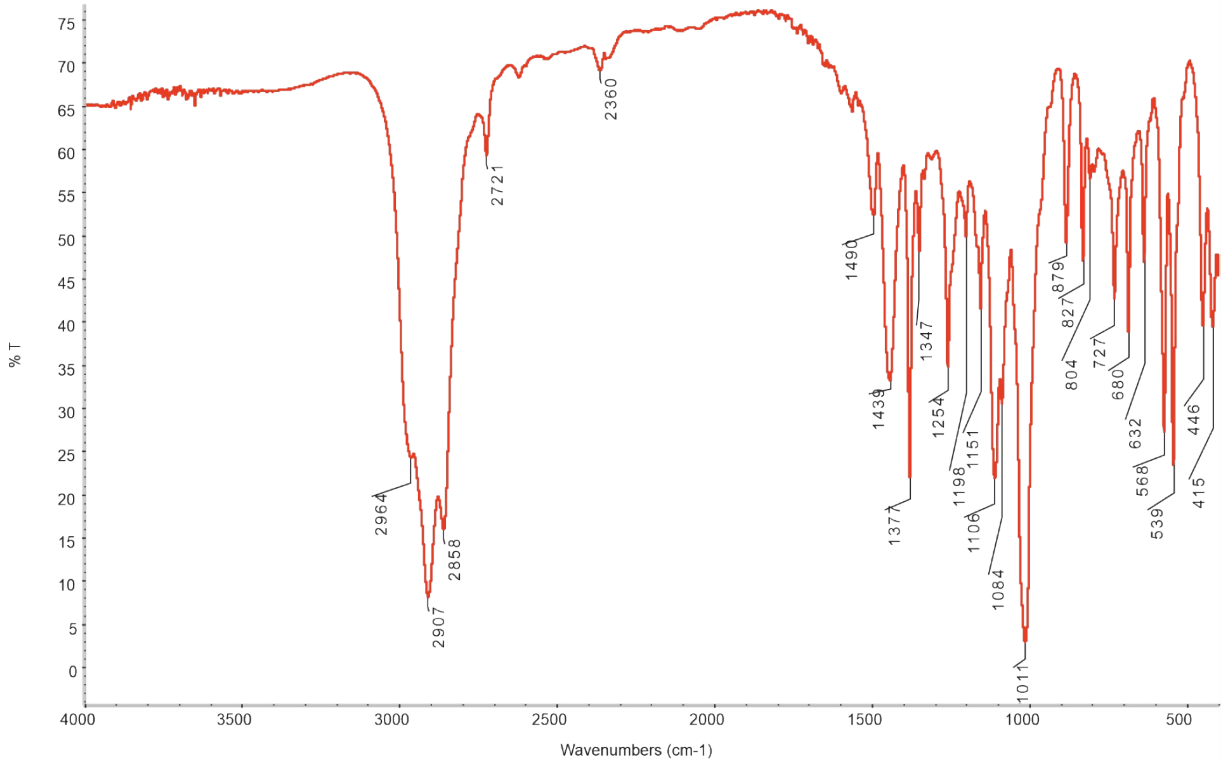
ESI Fig. 26. EPR spectrum of **10** in toluene at −160 °C. Features of major component in triplet state of orthorhombic symmetry are denoted (1), outer features of minor component are denoted (2).



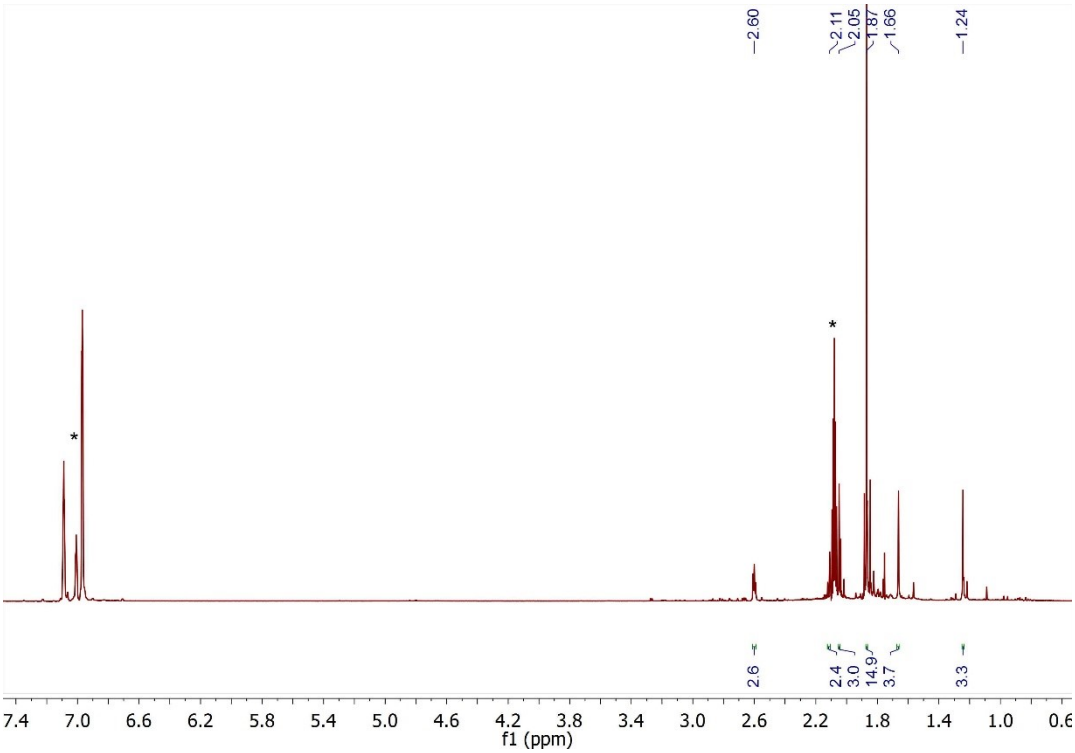
ESI Fig. 27. IR (KBr) spectrum of **10**.



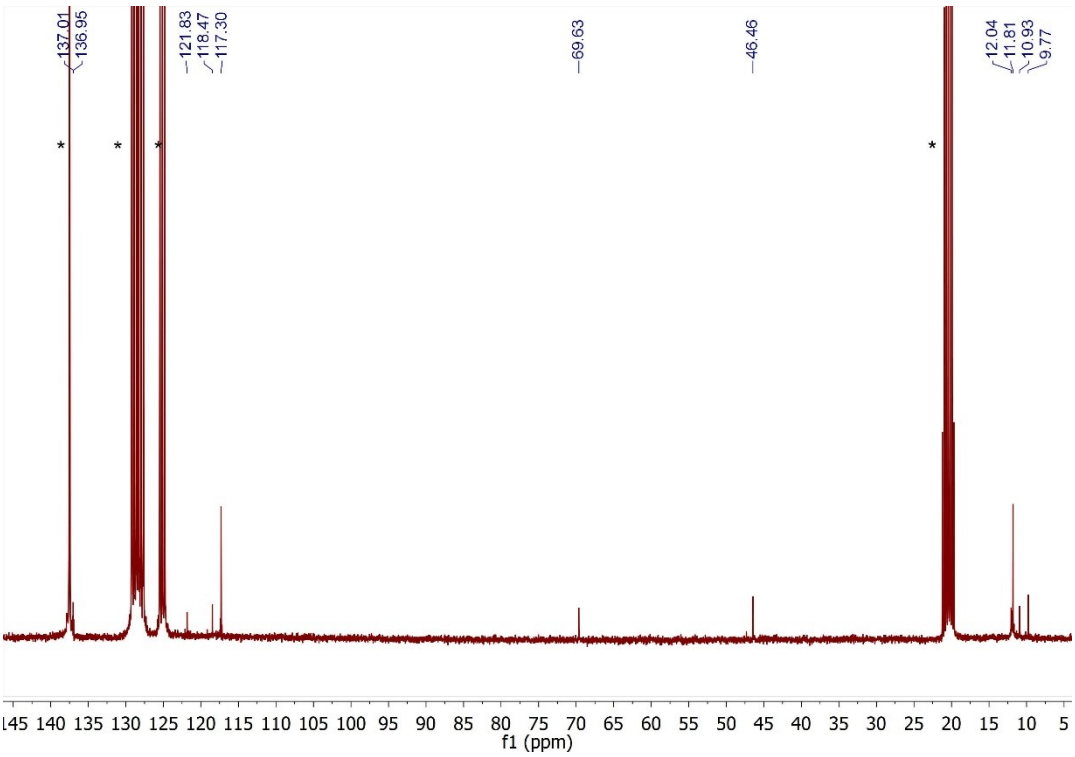
ESI Fig. 28. IR (KBr) spectrum of **12**.



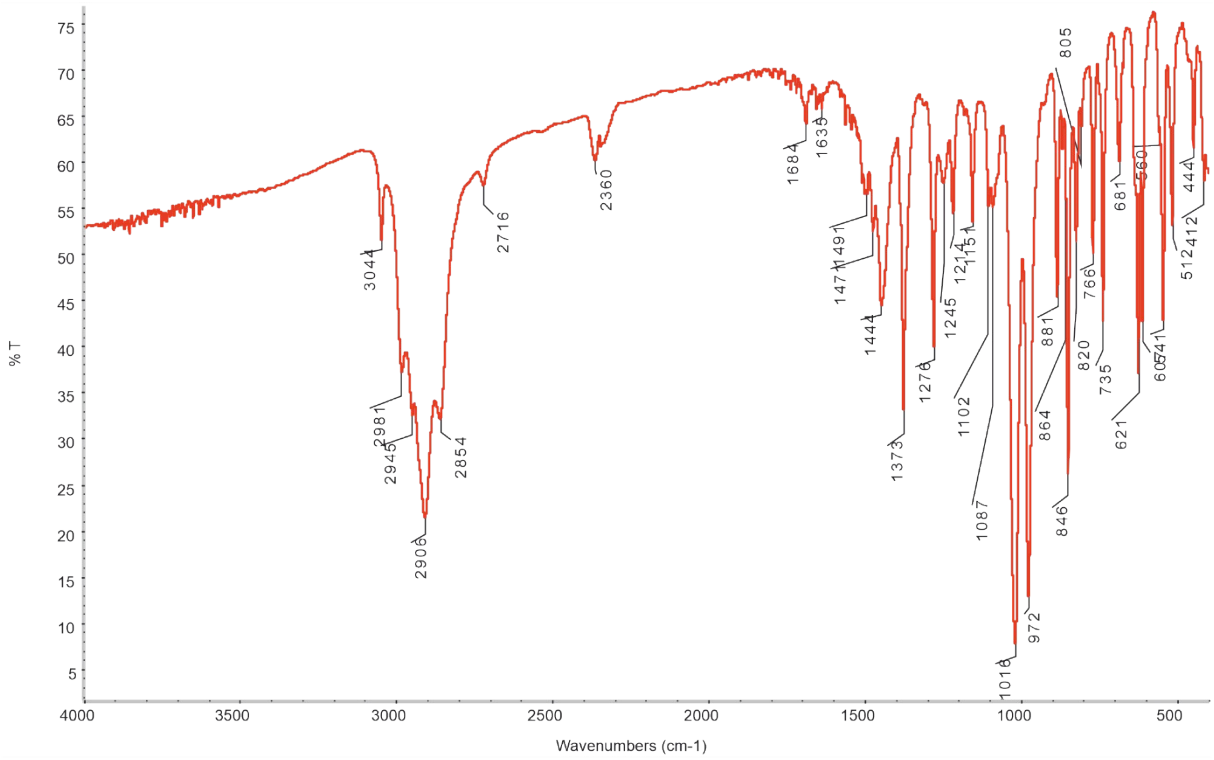
ESI Fig. 29. ^{1}H NMR spectrum of **13** in toluene-d_8. (*) denote residual signals of the solvent.



ESI Fig. 30. ^{13}C{^{1}H} NMR spectrum of **13** in toluene-d_8. (*) denote residual signals of the solvent.



ESI Fig. 31. IR (KBr) spectrum of **13**.



ESI Table 1. Crystallographic Data and Data Collection and Structure Refinement Details for Compounds **5**, **7**, **12**, and **13**.

	5	**7**	**13**	**12**
formula	$C_{24}H_{38}ClO_2SiTi$	$C_{21}H_{30}O_3Ti$	$C_{41}H_{56}O_2Ti_2$	$C_{41}H_{62}O_2Ti_2$
mol wt	469.98	378.35	676.65	682.70
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	16.0003(10)	13.3452(8)	14.8155(3)	8.6607(6)
b (Å)	10.4835(6)	14.1062(8)	15.1689(3)	12.4810(10)
c (Å)	15.7604(10)	10.0517(6)	15.7197(3)	18.5972(15)
α (°)	90	90	90	79.171(3)
β (°)	112.152(2)	94.620(2)	96.3290(10)	82.108(3)
γ (°)	90	90	90	71.927(3)
V (Å^3); Z	2448.5(3); 4	1886.09(19); 4	3511.23(12); 4	1870.3(3); 2
D_{calcd} (g cm^{-3})	1.275	1.332	1.280	1.212
μ (mm^{-1})	0.525	0.470	4.116	0.459
colour; habit	brown; prism	yellow; prism	orange; prism	red; prism
cryst size (mm^3)	0.772×0.604×0.436	0.514×0.462×355	0.564×0.362×0.286	0.979×0.491×0.172
T (K)	120(2)	150(2)	120(2)	120(2)
θ_{min}; θ_{max} (°)	2.380; 27.582	2.493; 27.494	3.001; 69.234	2.207; 27.541
range of h	−20→20	−17→17	−16→17	−11→11
range of k	−13→13	−18→18	−18→17	−15→16
range of l	−20→20	−13→13	−18→17	0→24
no. of diffrns collected	65126	33831	40839	8587
no. of unique diffrns	5635	4310	6444	8587
F(000)	1004	808	1448	736
no. of params	274	238	422	427
$R(F)$; $R_w(F^2)$ all data (%)	7.60; 15.88	3.87; 8.90	9.17; 16.14	5.81; 12.74
GOF (F^2), all data	1.246	1.062	1.056	1.085
$R(F)$; $R_w(F^2)$ (I > 2σ(I)) (%)	7.07; 15.71	3.25; 8.43	6.21; 14.17	5.02; 12.05
$\Delta\rho$ (e Å^{-3})	0.504; −0.718	0.299; −0.283	1.723; −1.151	1.584; −0.440