SUPPLEMENTARY MATERIALS (SM) FOR:

Synthesis and Reactivity of Poly(propyleneimine) Dendrimers Functionalized with Cyclopentadienone *N*-Heterocyclic-Carbene Ruthenium(0) Complexes

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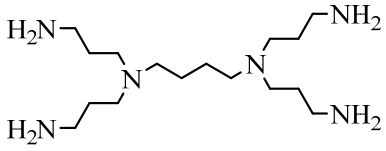
DAB-*dendr*-$(NH_2)_4$, g1:



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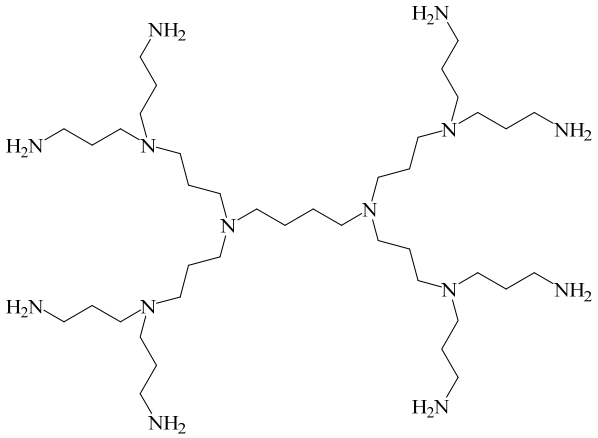

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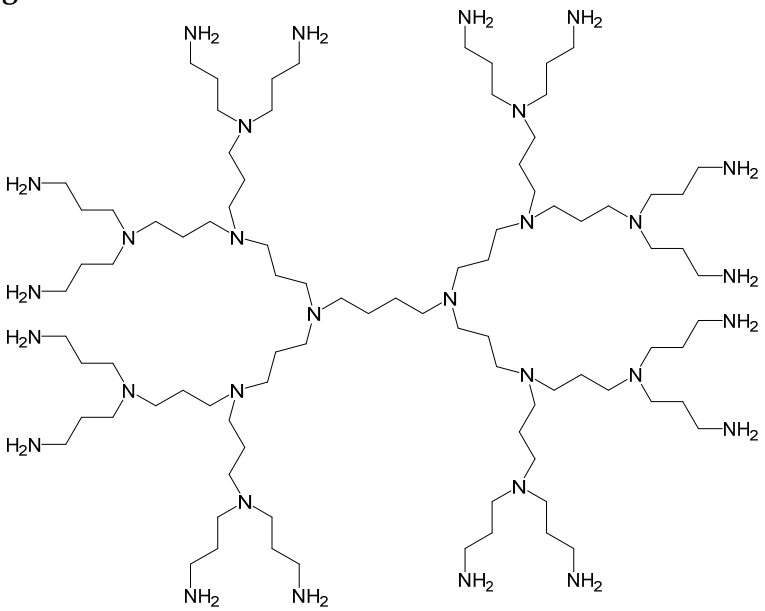

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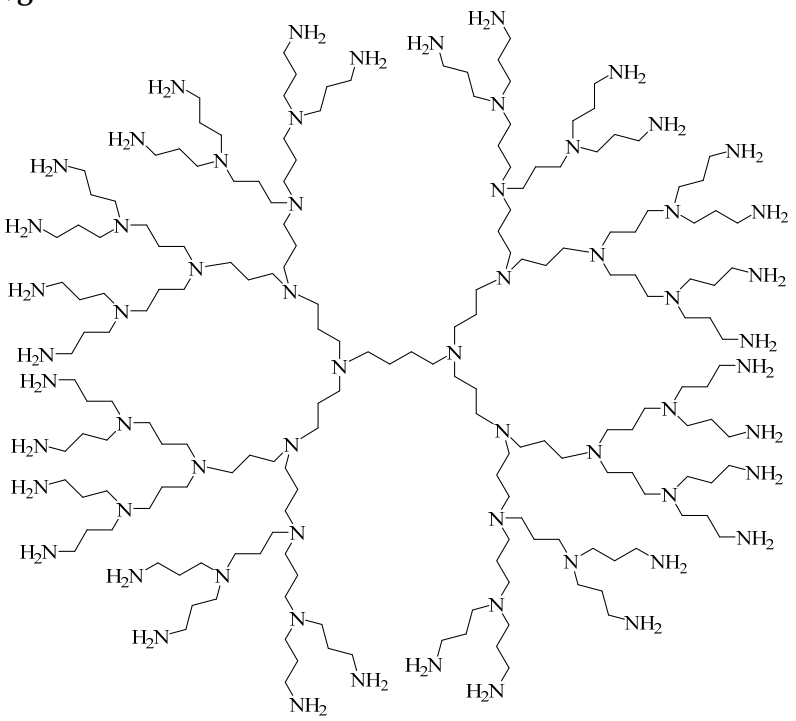
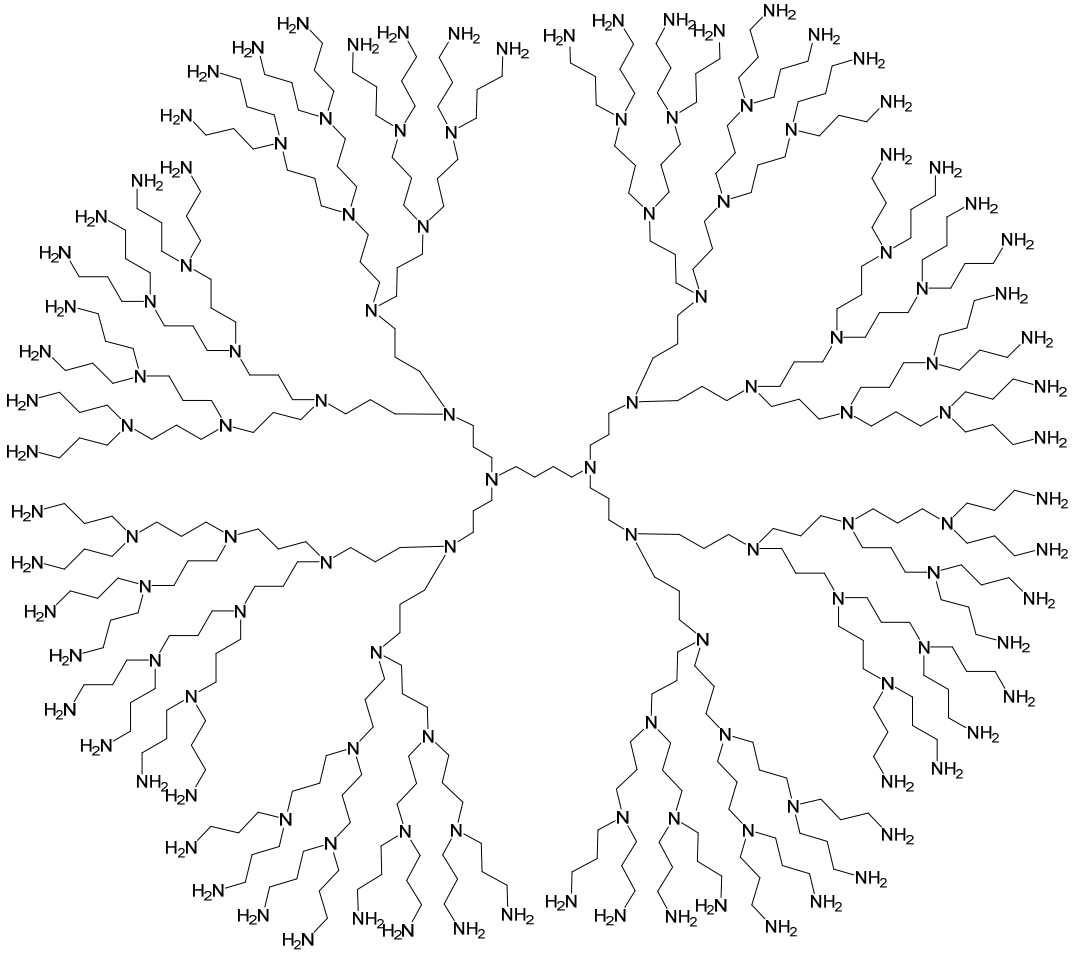
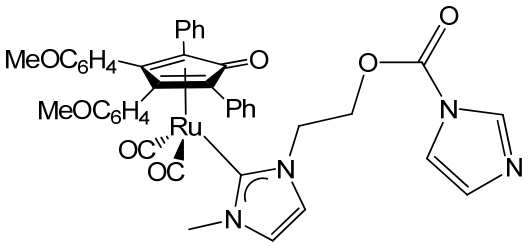


DAB-*dendr*-$(NH_2)_{64}$, g5:



Scheme S1. Polypropilenimine (PPIs) dendrimers **g1-5** used as support for ruthenium complexes in this work**.**

^{1}H and ^{13}C NMR, IR and MS-ESI characterization of ruthenium(0) complex 2



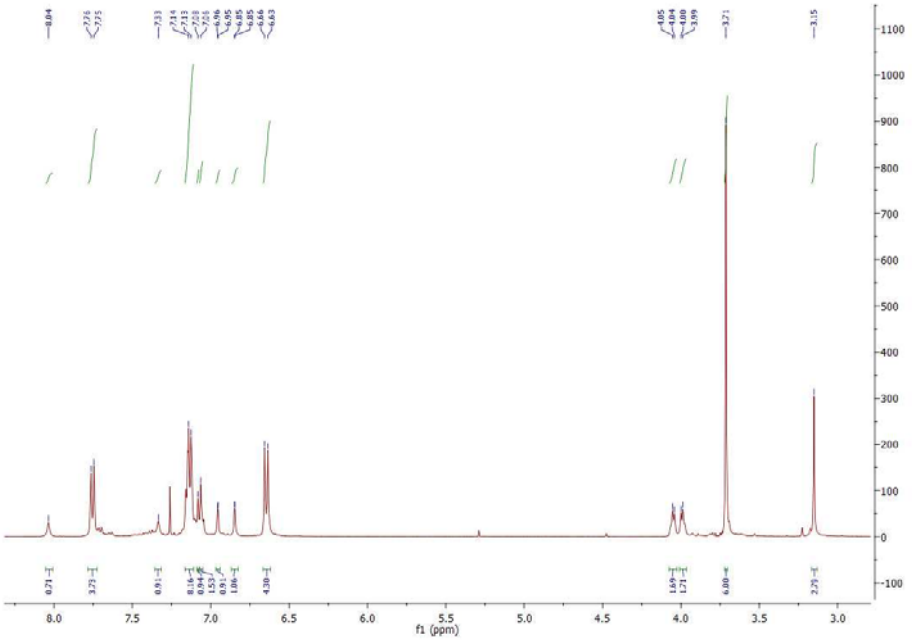


Figure S1. ^{1}H NMR spectrum of **2** in $CDCl_3$ (singlet at 5.3 ppm is given by CH_2Cl_2).

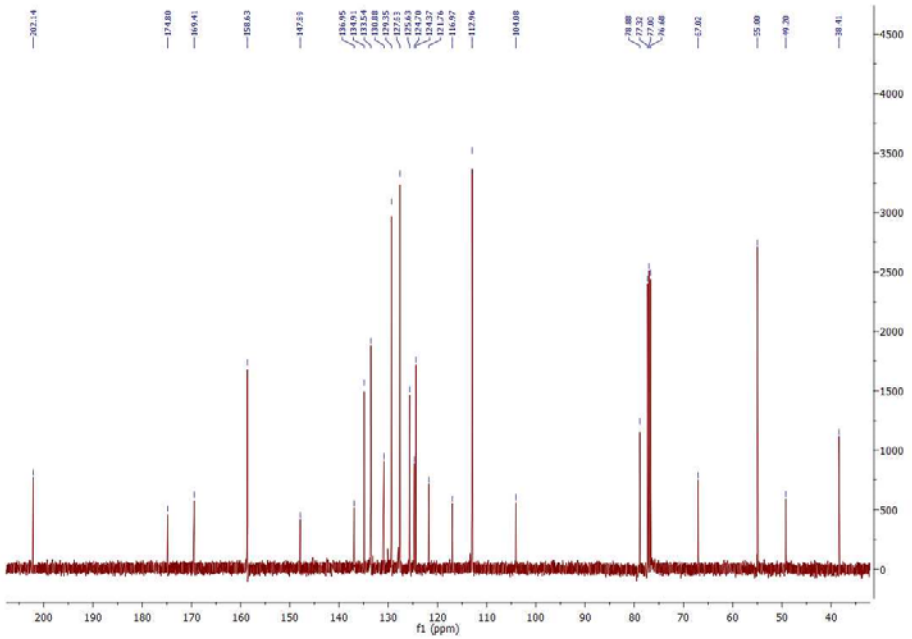


Figure S2. ^{13}C NMR spectrum of **2** in $CDCl_3$.

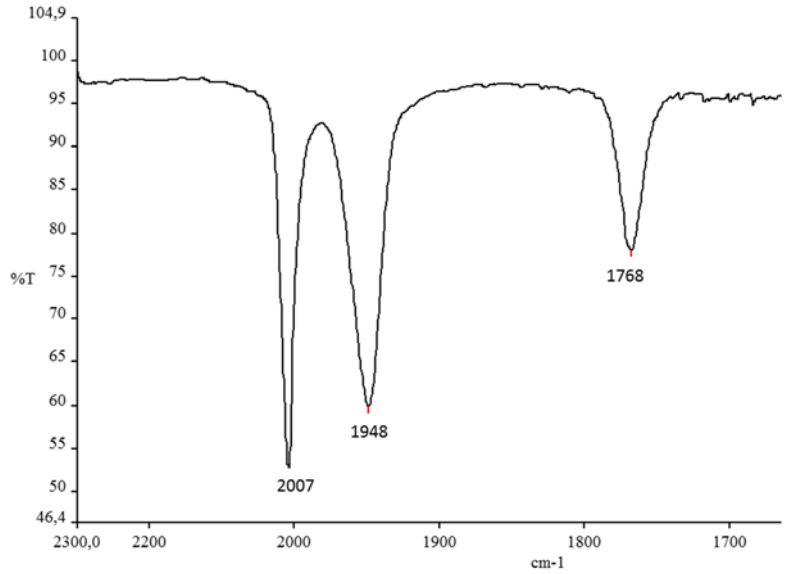


Figure S3. FT-IR spectrum of **2** (carbonyl CO and C=O region) in CH_2Cl_2.

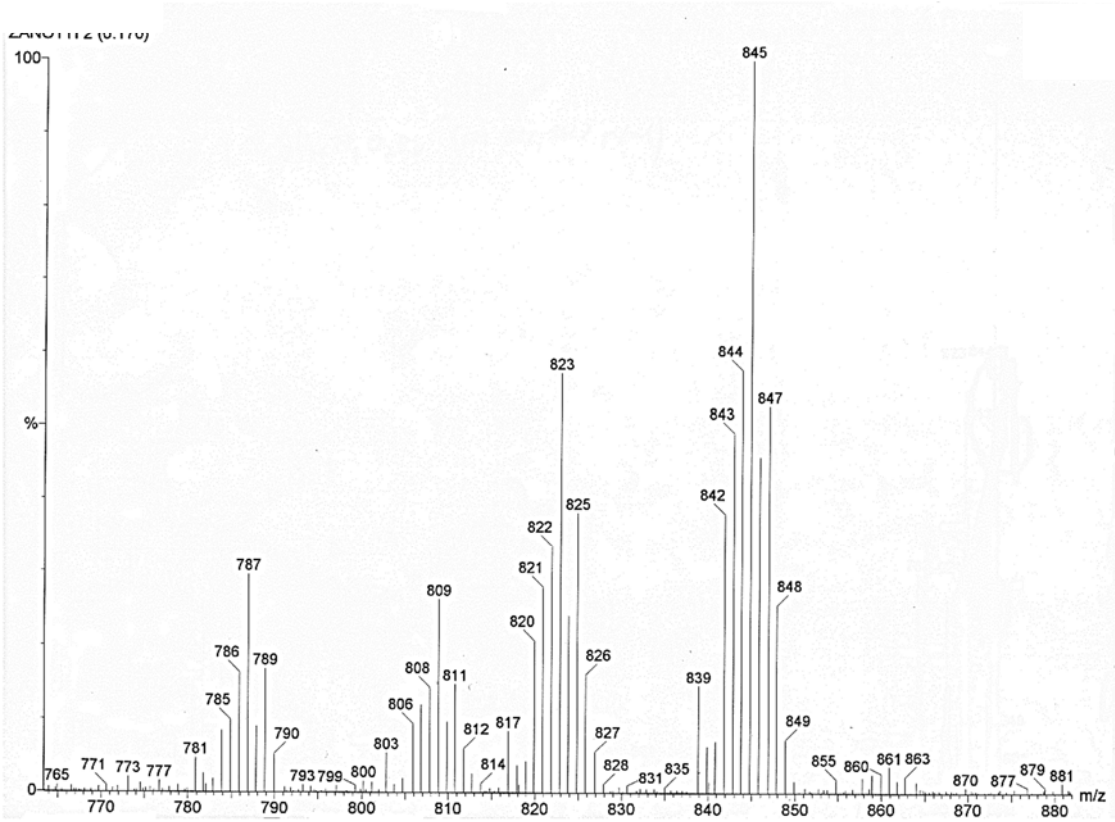
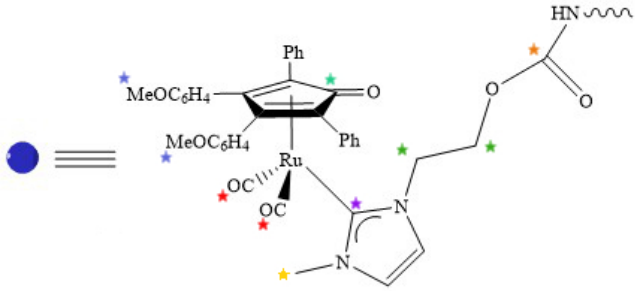
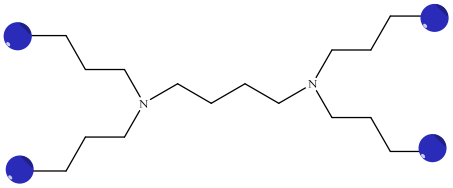


Figure S4. MS-ESI+ spectrum of **2**.

^{1}H and ^{13}C NMR of functionalized neutral dendrimers



3g1



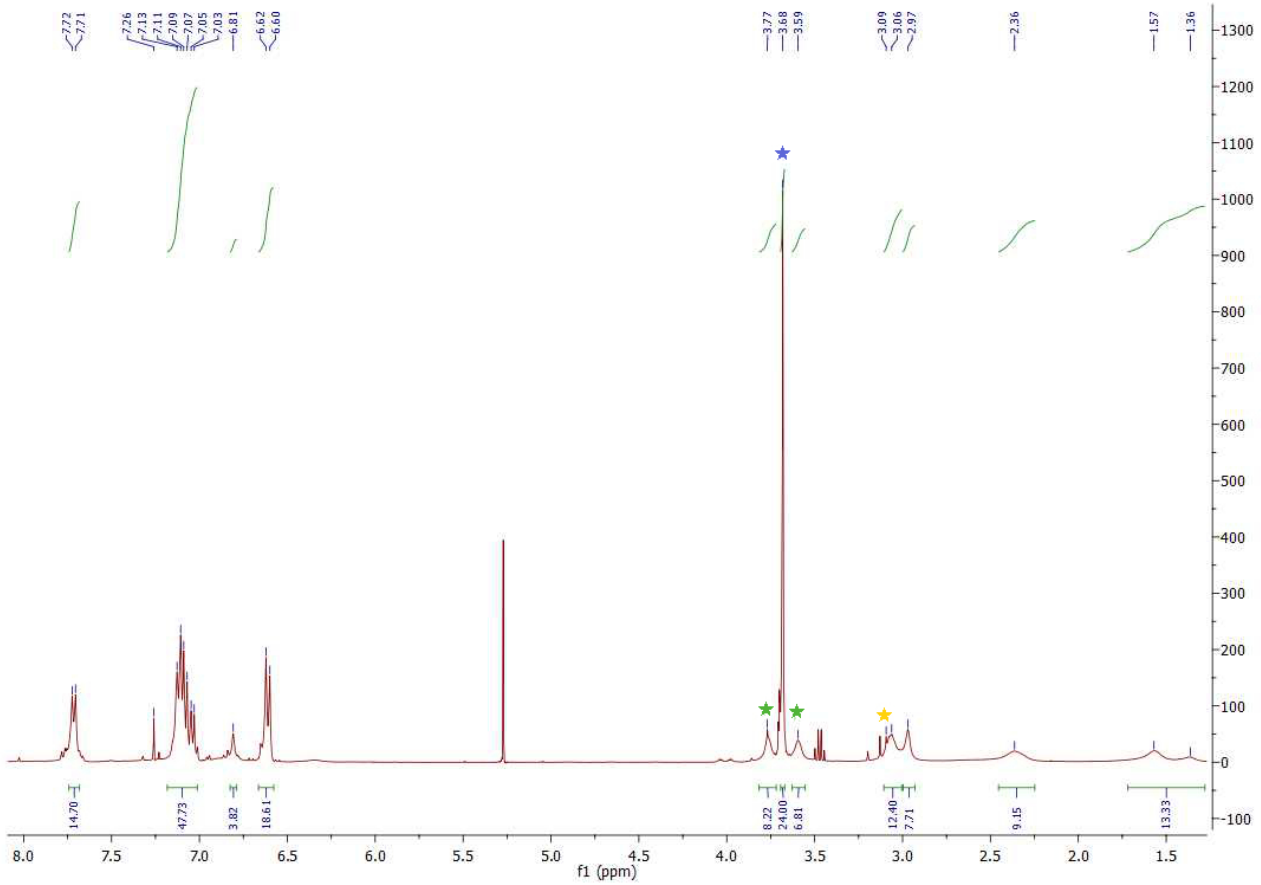


Figure S5. ^{1}H NMR spectrum of **3g1** in $CDCl_3$ (singlet at 5.3 ppm is given by CH_2Cl_2).

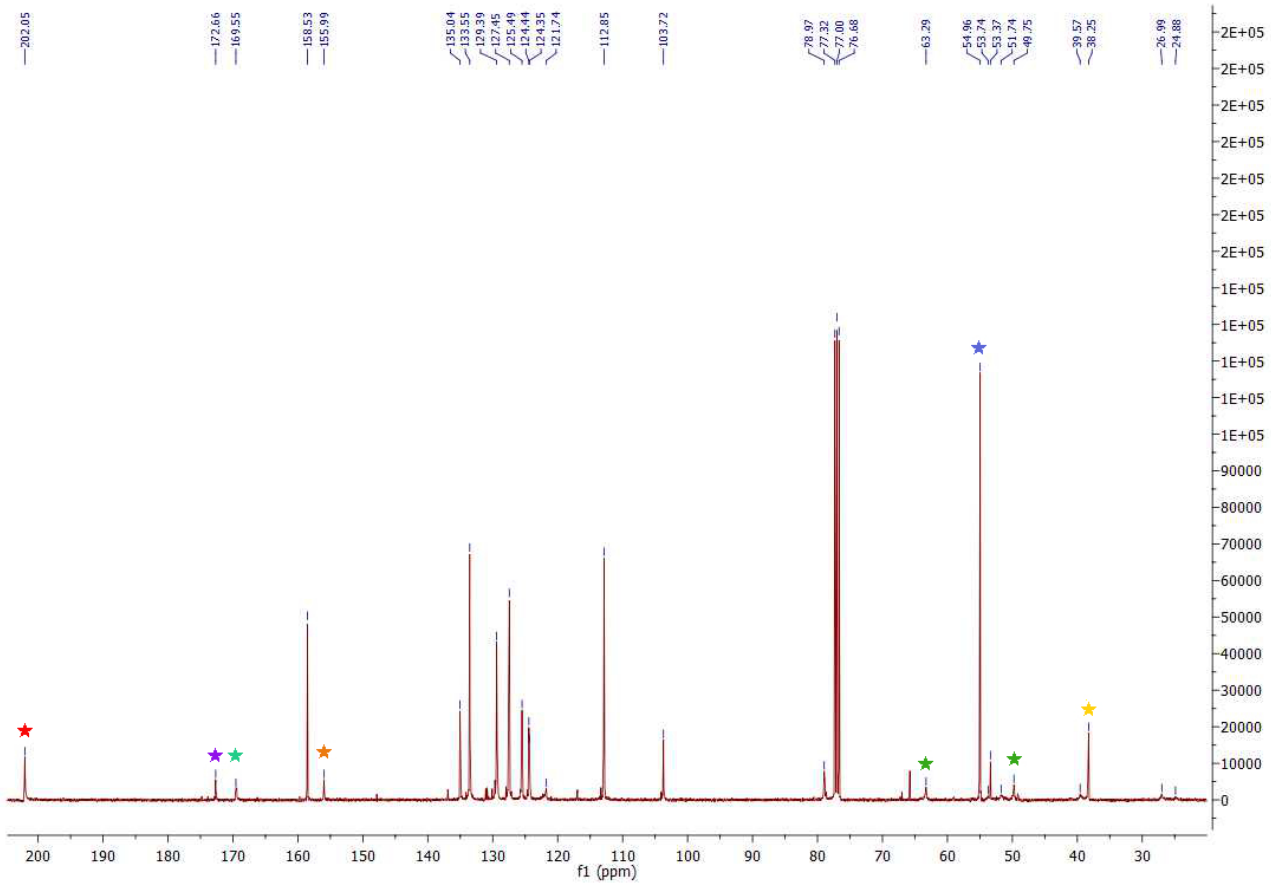


Figure S6. ^{13}C NMR spectrum of **3g1** in $CDCl_3$.

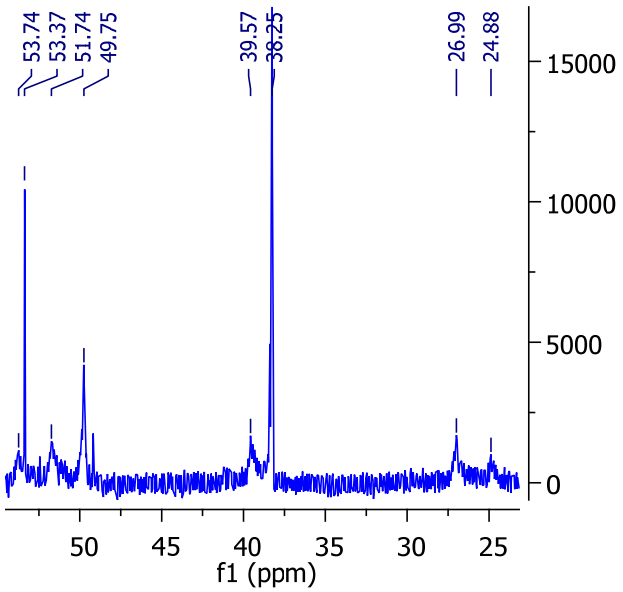


Figure S7. ^{13}C NMR spectrum of **3g1**: expanded zone in which CH_2 moieties of the branched dendrimers appear.

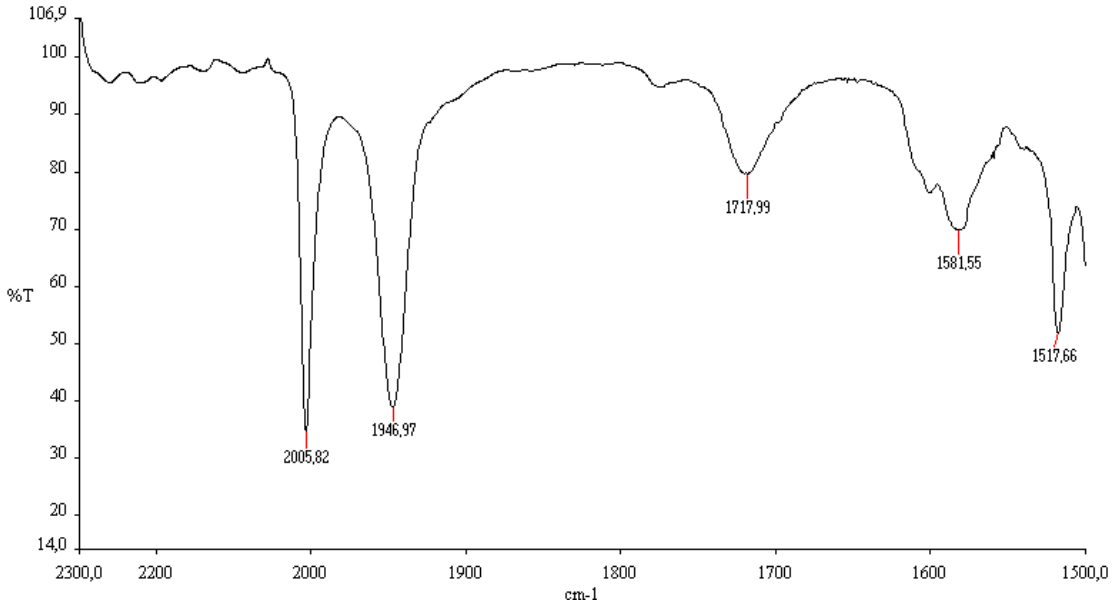


Figure S8. FT-IR spectrum of **3g1** (terminal CO and C=O zone) in CH_2Cl_2. FT-IR spectra of **3g2**-**3g5** are practically superimposable to this one, so they will be omitted.

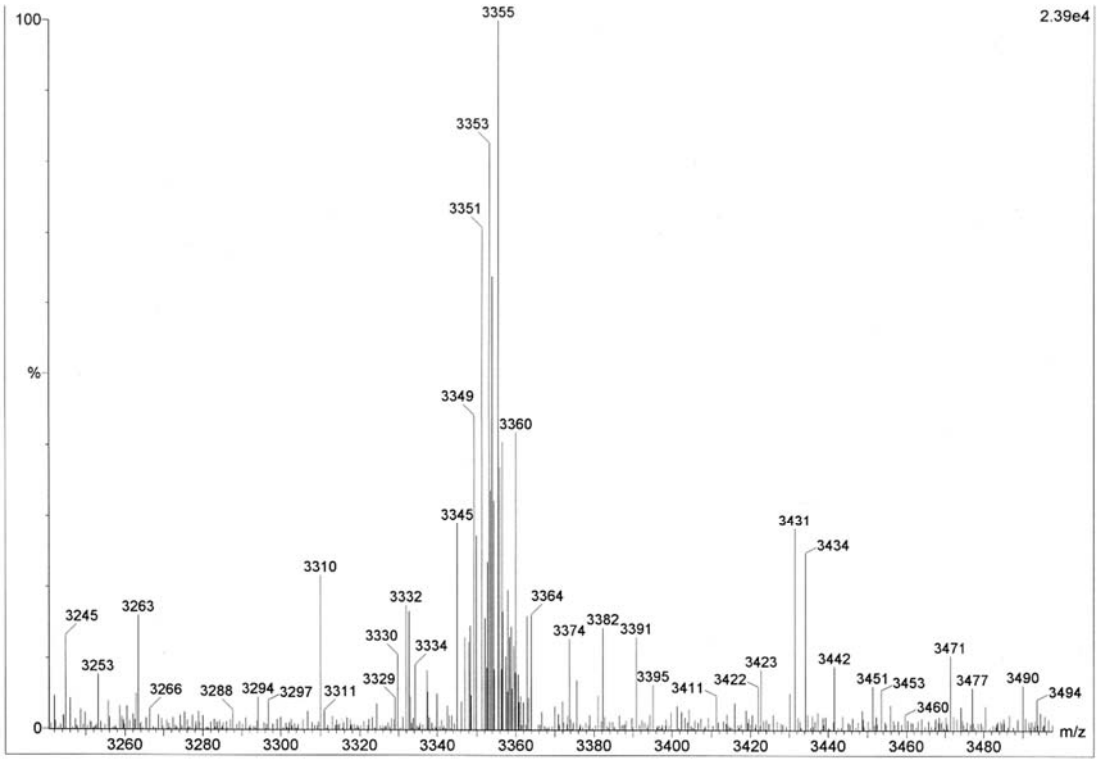
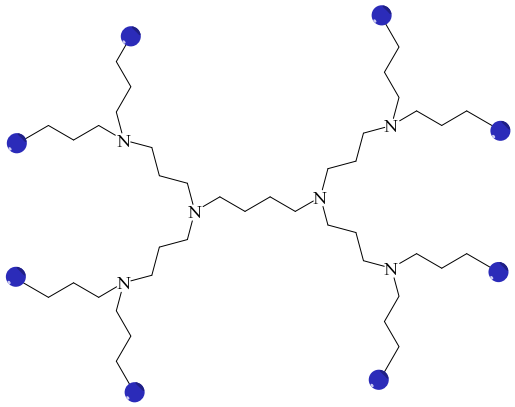


Figure S9. MS-ESI+ spectrum of **3g1**. Mass spectra of the higher generations **3g2**-**3g5** exceeds the maximum molecular weight allowed for the techniques available.

3g2



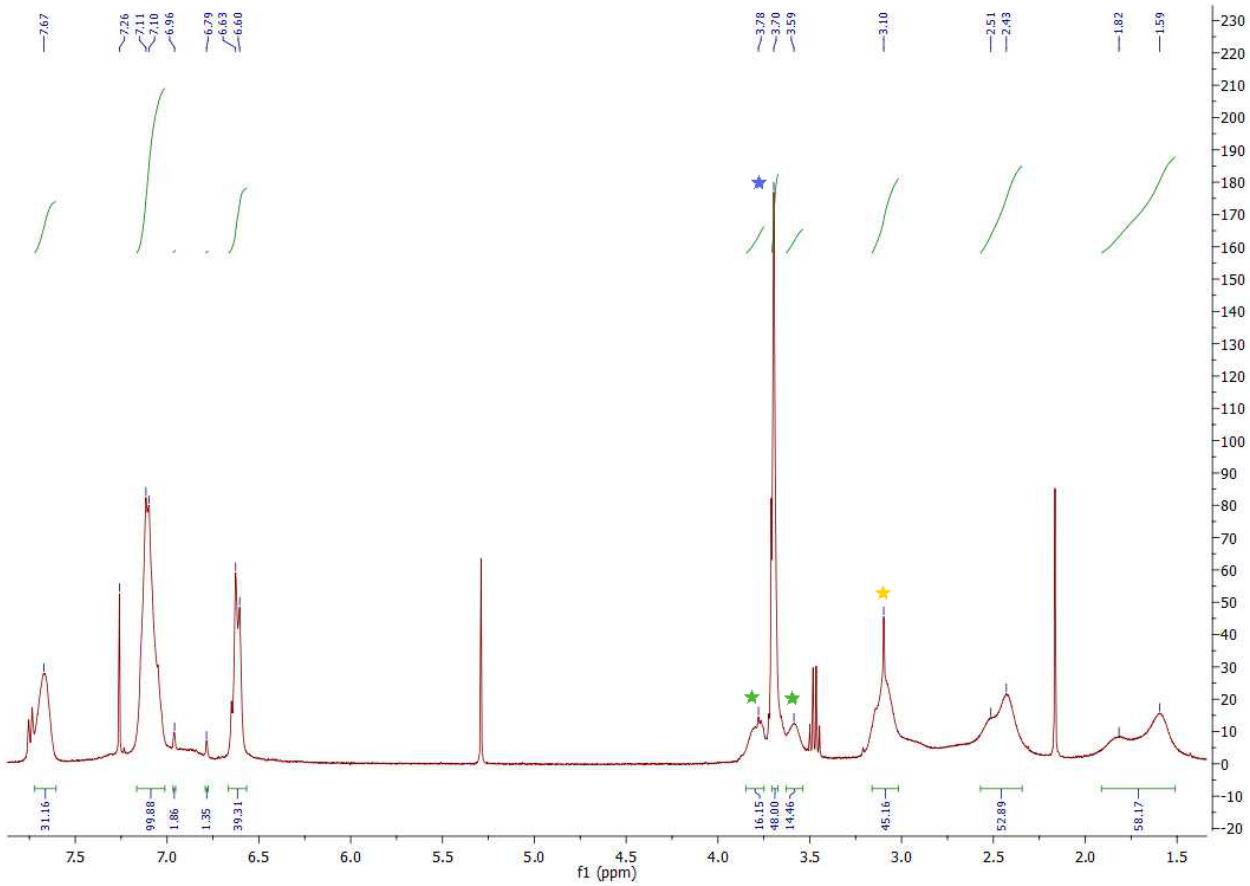


Figure S10. ^{1}H NMR spectrum of **3g2** in $CDCl_3$ (singlet at 5.3 ppm is given by CH_2Cl_2).

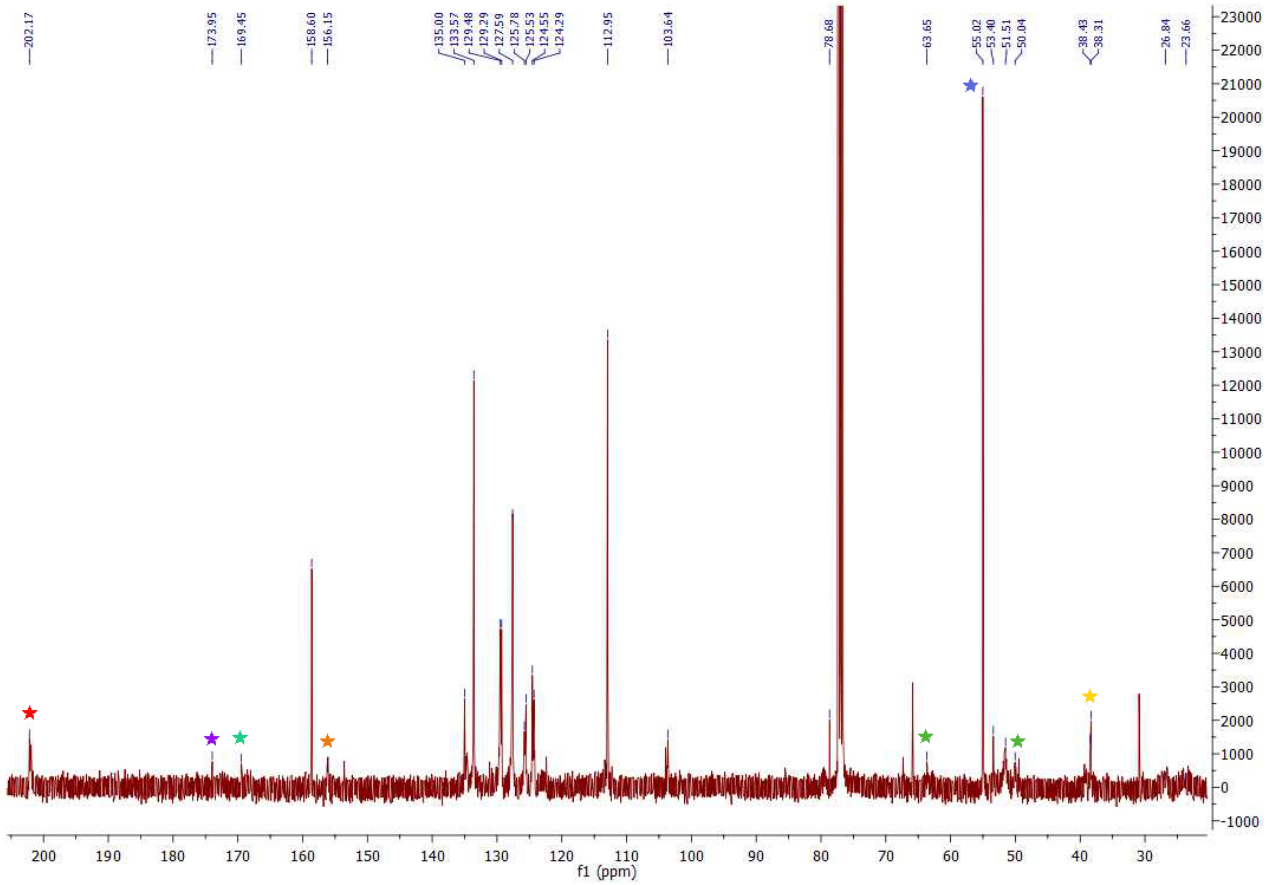


Figure S11. ^{13}C NMR spectrum of **3g2** in $CDCl_3$.

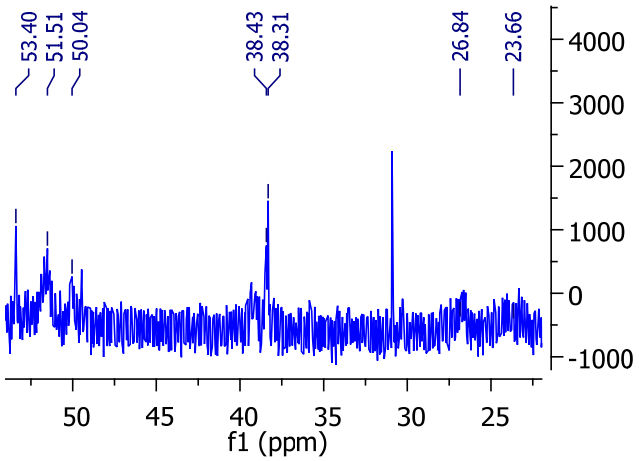


Figure S12. ^{13}C NMR spectrum of **3g2**: expanded zone in which CH_2 moieties of the branched dendrimers appear.

3g3

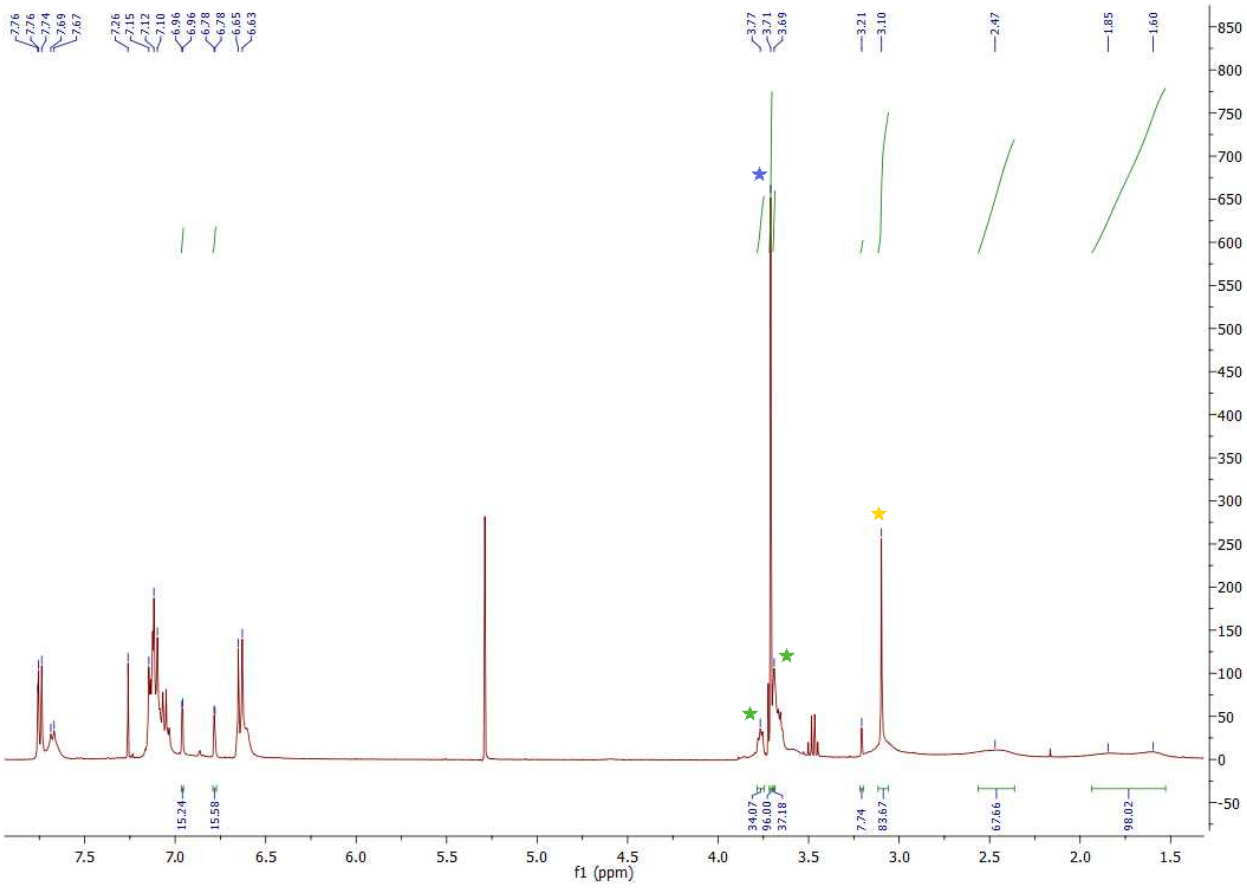


Figure S13. ^{1}H NMR spectrum of **3g3** in $CDCl_3$ (singlet at 5.3 ppm is given by CH_2Cl_2).

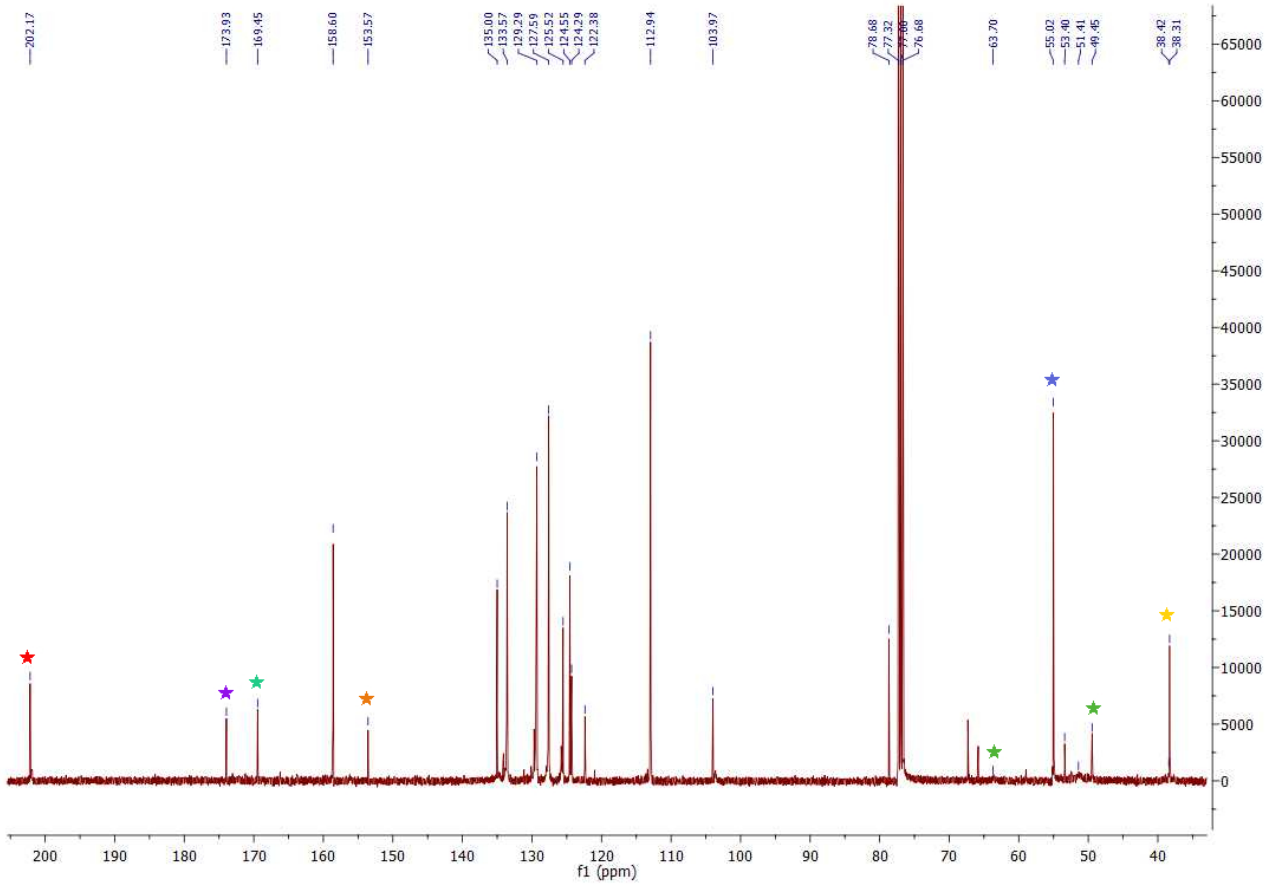


Figure S14. ^{13}C NMR spectrum of **3g3** in $CDCl_3$.

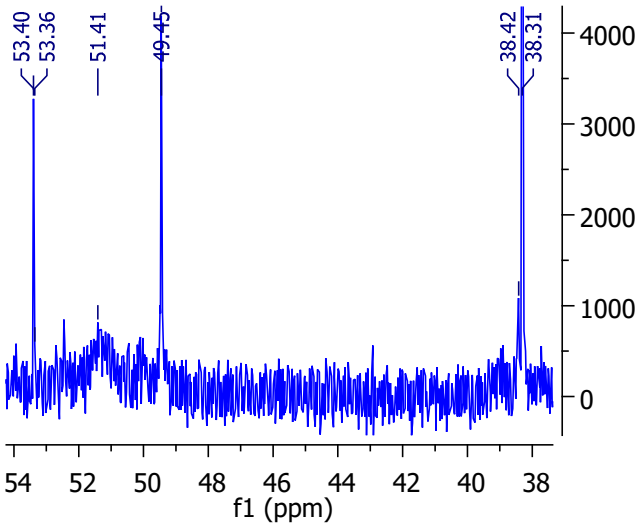


Figure S15. ^{13}C NMR spectrum of **3g3:** expanded zone in which CH_2 moieties of the branched dendrimers appear.

3g4

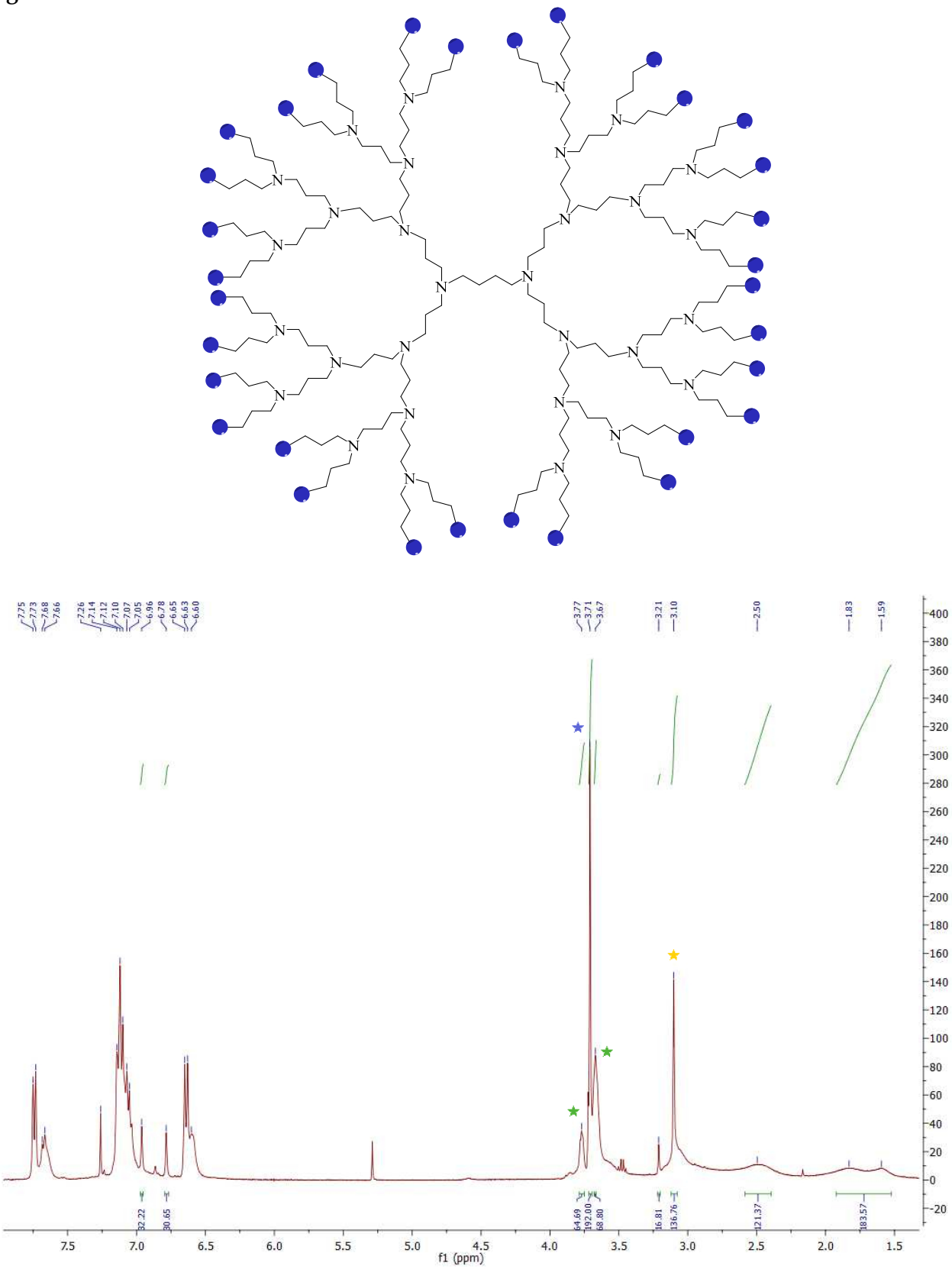


Figure S16. ^{1}H NMR spectrum of **3g4** in $CDCl_3$ (singlet at 5.3 ppm is given by CH_2Cl_2).

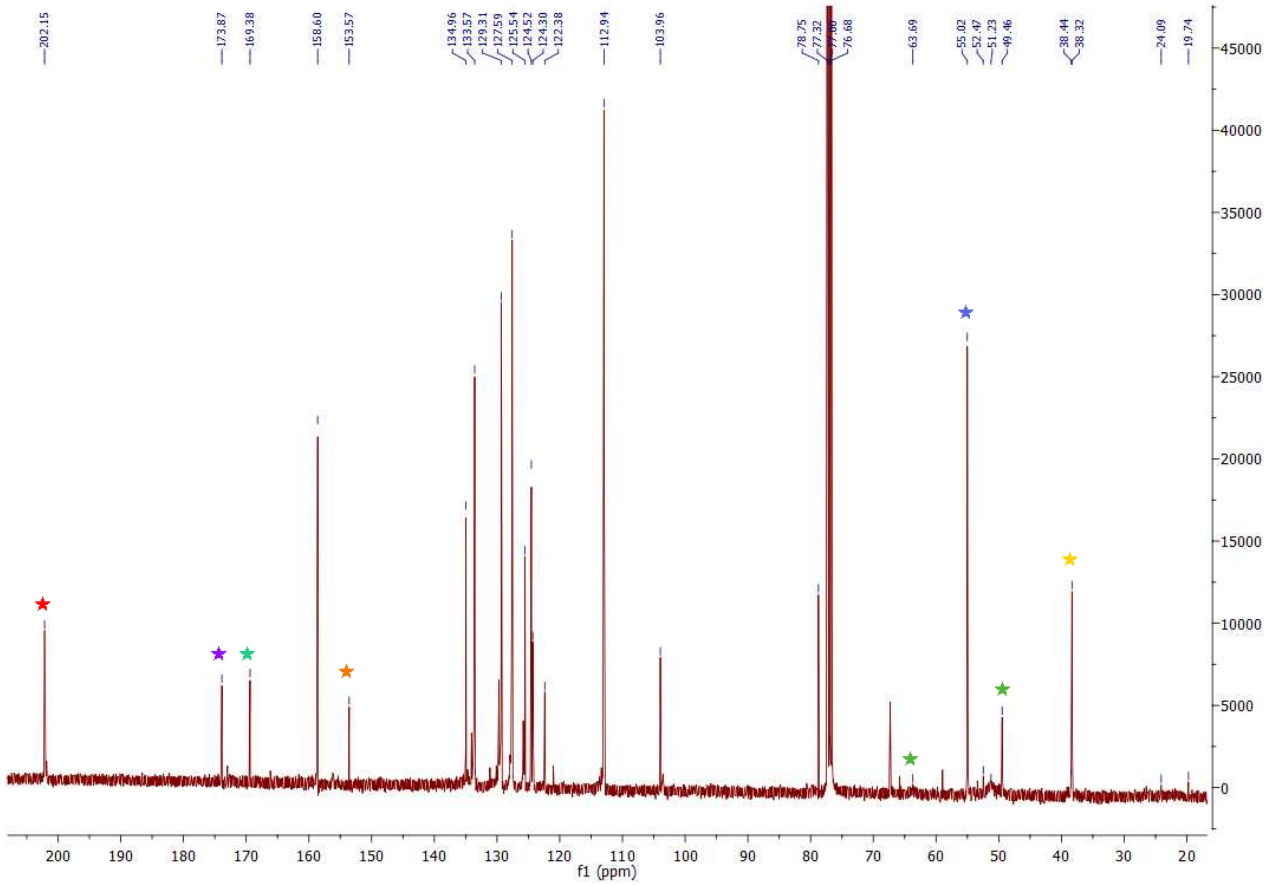


Figure S17. ^{13}C NMR spectrum of **3g4** in $CDCl_3$.

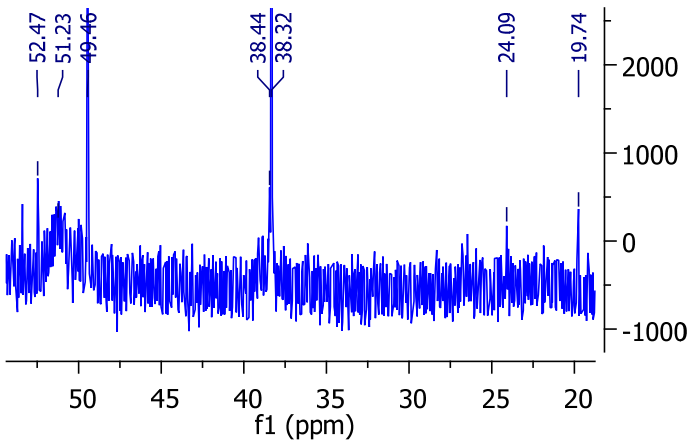
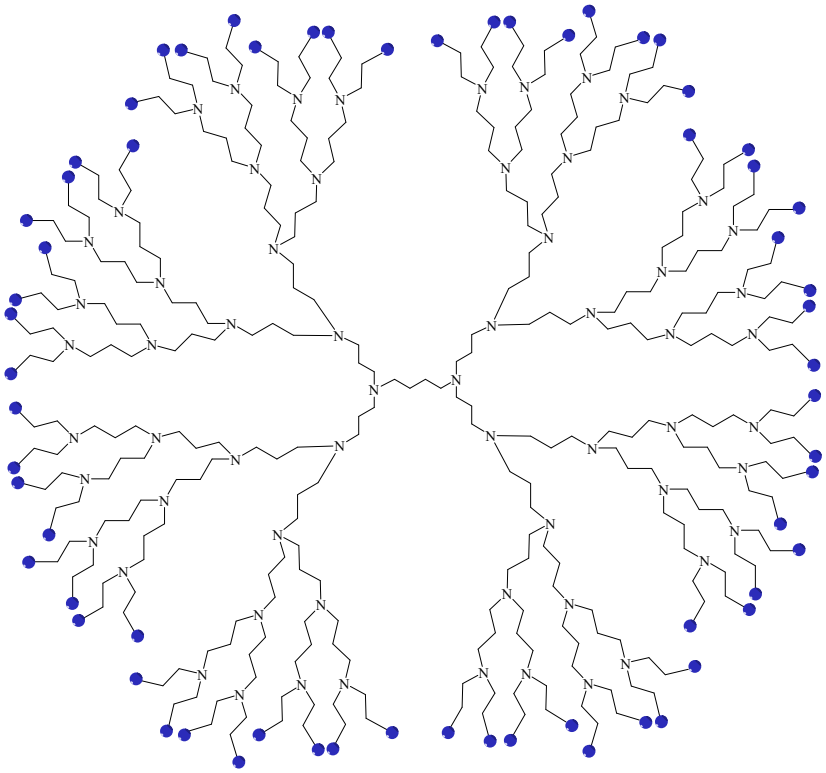


Figure S18. ^{13}C NMR spectrum of **3g4**: expanded zone in which CH_2 moieties of the branched dendrimers appear.

3g5



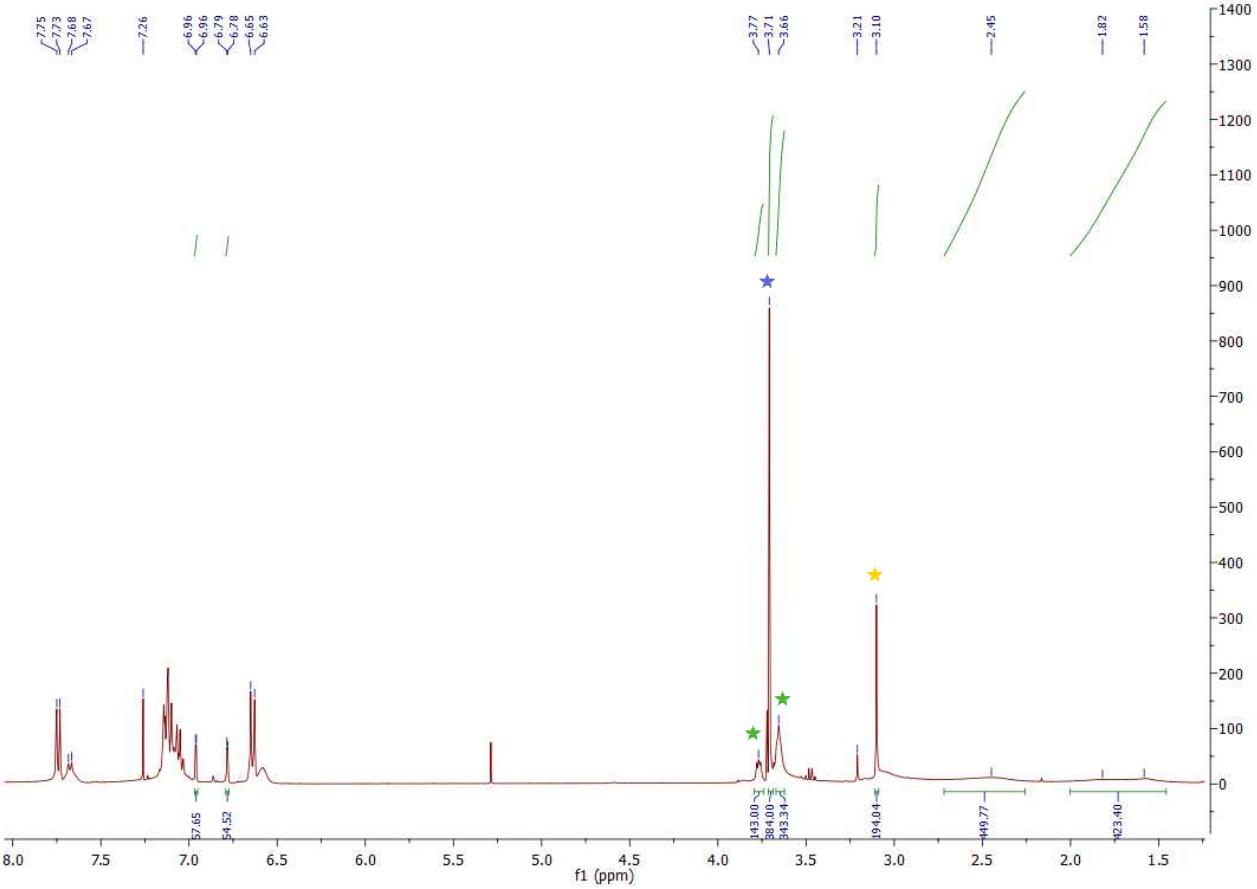


Figure S19. ^{1}H NMR spectrum of **3g5** in $CDCl_3$ (singlet at 5.3 ppm is given by CH_2Cl_2).

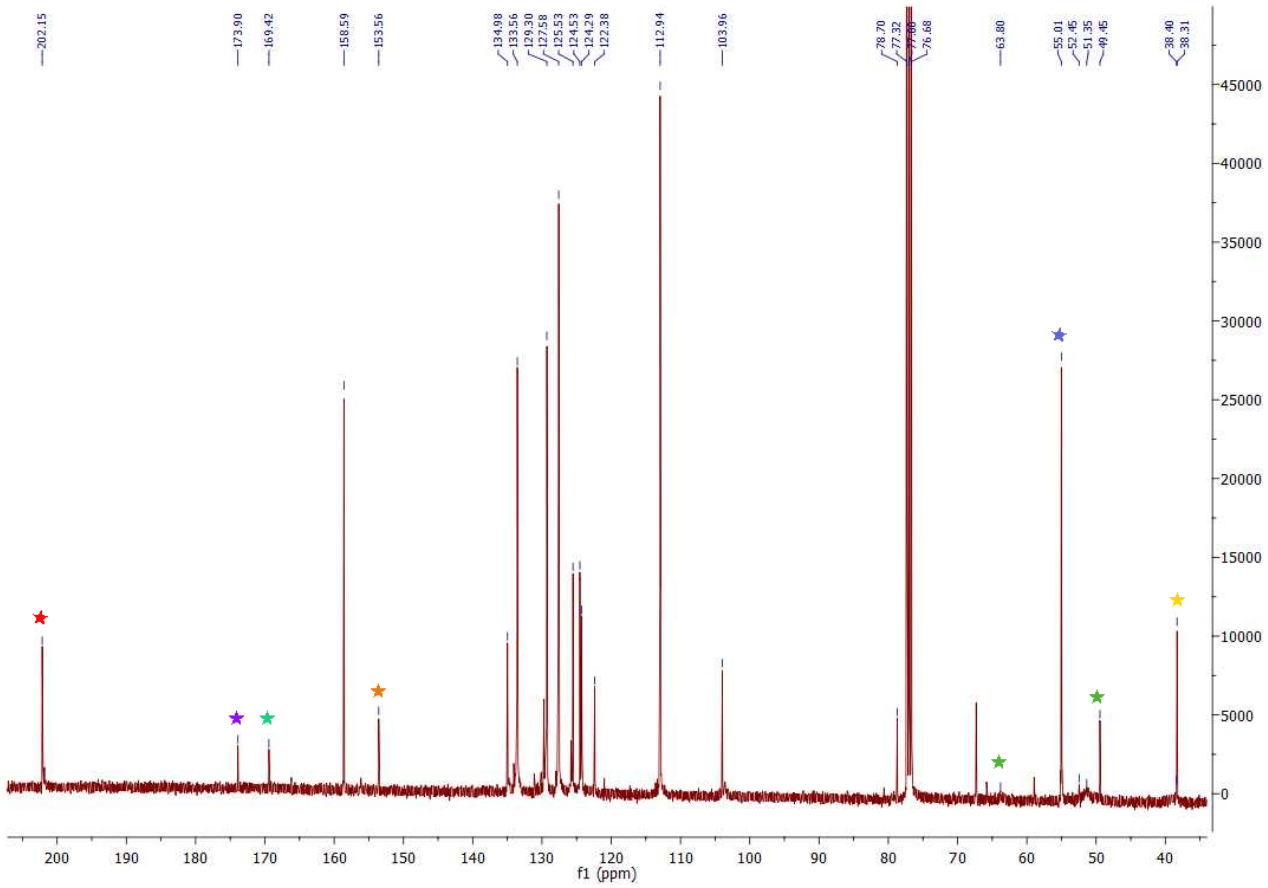


Figure S20. ^{13}C NMR spectrum of **3g5** in $CDCl_3$.

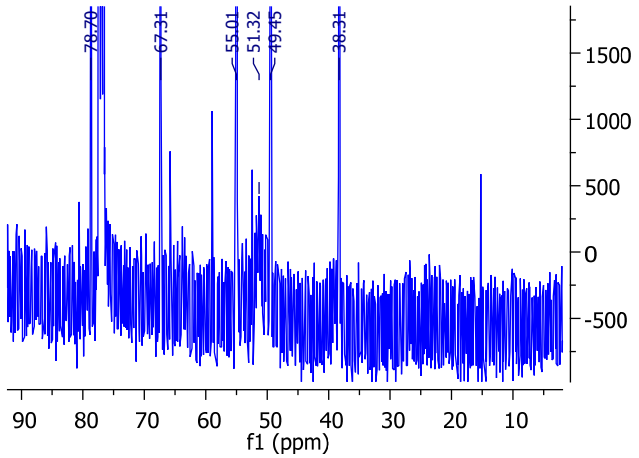


Figure S21. ^{13}C NMR spectrum of **3g5**: expanded zone in which CH_2 moieties of the branched dendrimers appear.

Time-conversion profile for 3g1 + CAN (1 eq.).

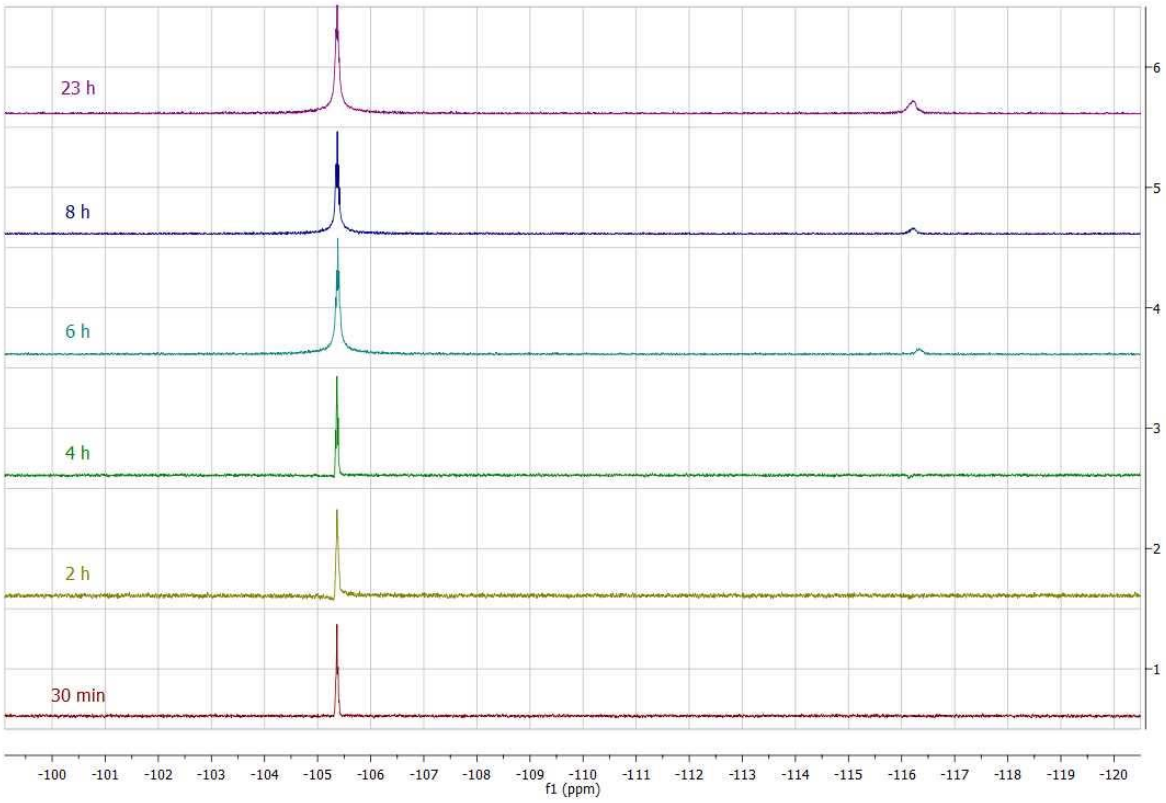


Figure S22. ^{19}F NMR acquired on samples taken at different reaction times (30 min, 2 h, 4 h, 6 h, 8 h, 23 h) using **3g1** as catalyst and CAN as additive.

Table S1. Yields at different reaction times calculated using ^{19}F NMR spectra of **Figure S22**.

t [min]	Yield(%)
0	0
30	0
120	0
240	5
360	7
480	9
1380	17

Time-conversion profile for 3g1 + pyridine (10 eq.).

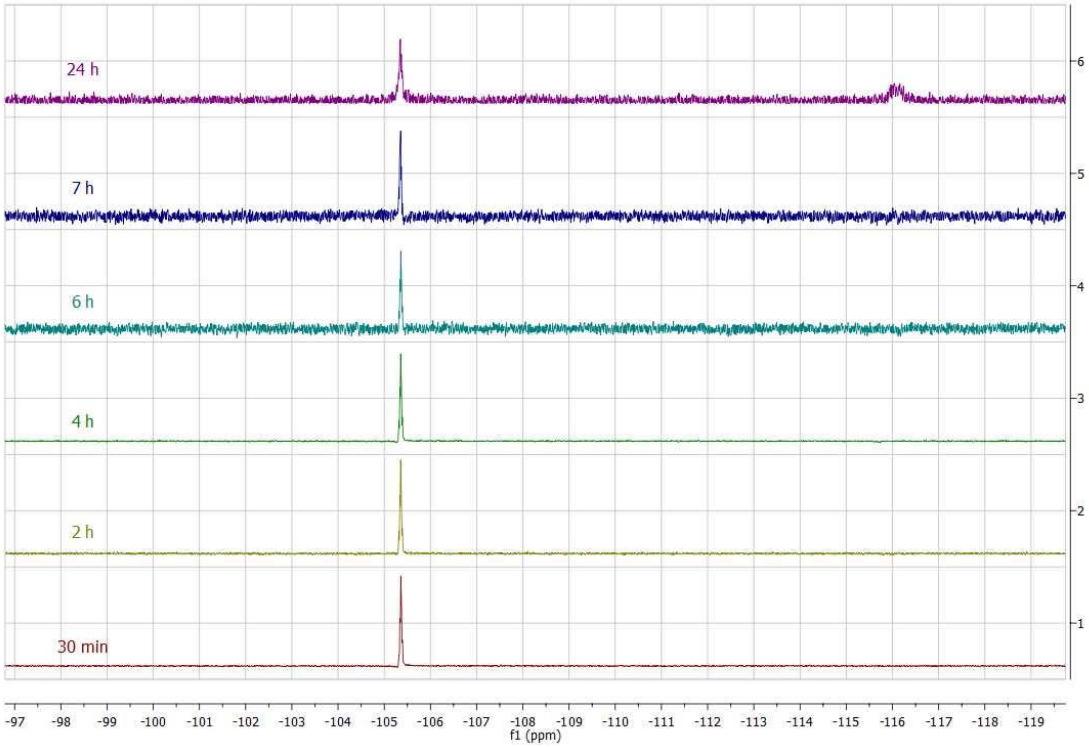


Figure S23. ^{19}F NMR acquired on samples taken at different reaction times (30 min, 2 h, 4 h, 6 h, 7 h, 24 h) using **3g1** as catalyst and pyridine as additive.

Table S2. Yields at different reaction times calculated using ^{19}F NMR spectra of **Figure S23**.

t [min]	Yield
0	0
30	0
120	0
240	0
360	0
420	0
1380	20