Electronic Supplementary Material (ESI) for RSC Advances.

Aryl Tosylates as Non-Ionic Photoacid Generators (PAGs). Photochemistry and Applications in Cationic Photopolymerizations

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Supporting Information

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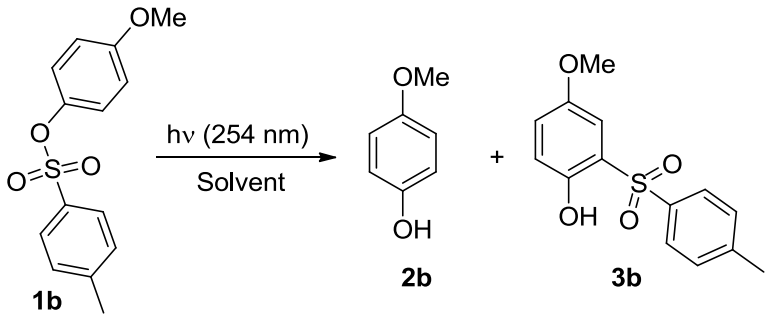
1. Photophysical and photochemical data of aryl tosylates 1a-g.

Table S1: Photophysical and photochemical data of aryl tosylates 1a-g in neat methanol.

ArOTs	ε/L (mol^{-1} cm^{-1})[a]	λ_{em}, $\Phi_F \times 10^{-2}$	Φ_{-1} [b]
1a	7400	378, 0.31	0.11
1b	1826	344, 0.92	0.14
1c	1131	-	0.14
1d	18900	-	0.29
1e	5510	-	< 0.01
1f	2450	-	0.11
1g	1460	-	0.21

[a] Molar absorption coefficient at 254 nm. [b] Disappearance quantum yield measured on a 10^{-2} M **1a-g** solution in MeOH (λ = 254 nm, 1×15W Hg lamp) by using potassium ferrioxalate as actinometer.

Table S2. Irradiation of Aryl Tosylate 1b in Neat Solvents[a]



Solvent	C-H BDE (kcal mol^{-1})[b]	E^N_T[c]	2b (%)	3b (%)
Cyclohexane	97.6	0.006	4	68
CH_2Cl_2, Φ_{-1} = 0.08[d]	97.3 ± 1.0	0.309	12	33
$CH_3COOCH_2CH_3$	95.4	0.228	26	36
THF	92 ± 1	0.207	39	24
CH_3CN, Φ_{-1} =0.13[d]	96	0.460	24	30
$CH_3OCH_2CH_2OH$, Φ_{-1} = 0.07[d]	-	0.657	34	29
CH_3OH, Φ_{-1} = 0.14[d]	95.9 ±1.5	0.762	41	28

[a] A nitrogen saturated solution of **1b** (10^{-2} M) in the chosen solvent irradiated at 254 nm (4×15 W Hg lamps) until a >80% consumption of **1b** was achieved (2h). Product yields calculated on the basis of the amount of **1b** consumed. [b] from Luo, Y-R.; Handbook of Bond Dissociation Energies in Organic Compounds, CRC Press , Boca Raton, Florida, 2003 [c] Relative polarity, from Christian Reichardt, Solvents and Solvent Effects in Organic Chemistry, Wiley-VCH Publishers, 3rd ed., 2003. [d] Disappearance quantum yield (Φ_{-1}) measured on a 10^{-2} M **1b** solution in the chosen solvent (λ = 254 nm, 1×15W Hg lamp) by using potassium ferrioxalate as actinometer.

UV-vis spectra of compounds 1a-g.

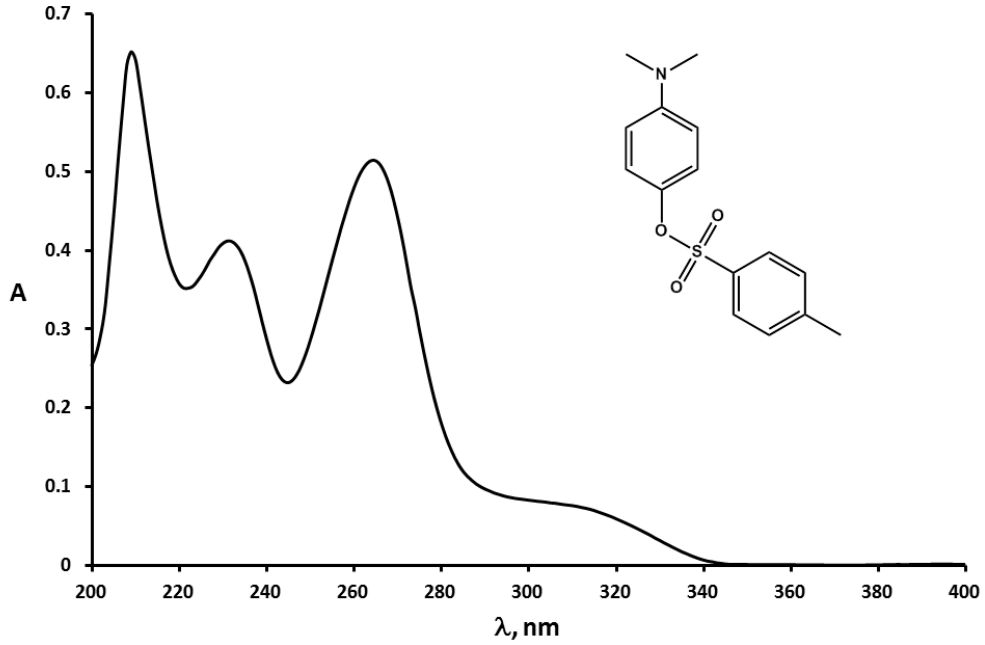


Figure S1. UV-vis spectrum of **1a** (5×10^{-5} M) in MeOH.

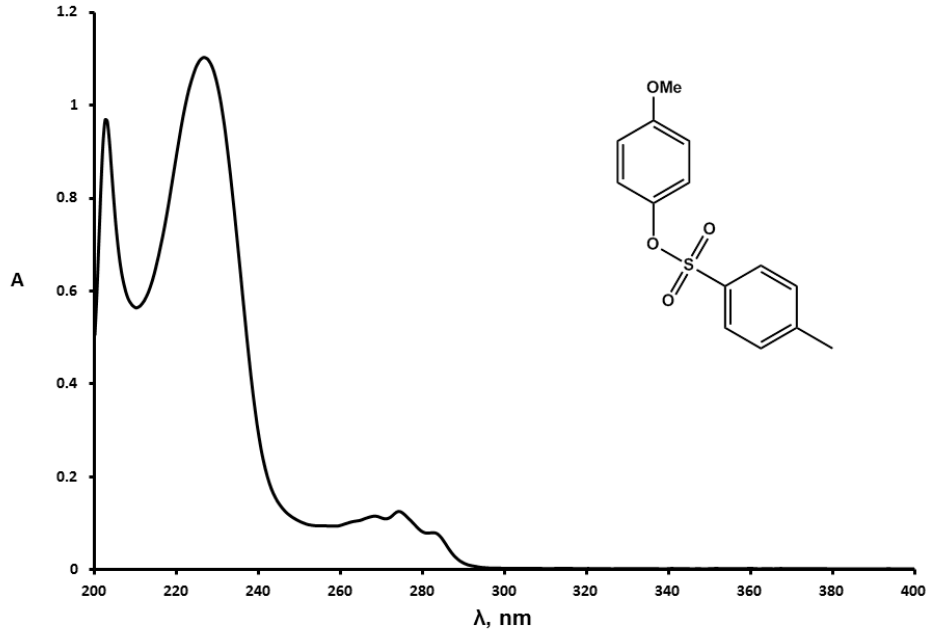


Figure S2. UV-vis spectrum of **1b** (5.2×10^{-5} M) in MeOH.

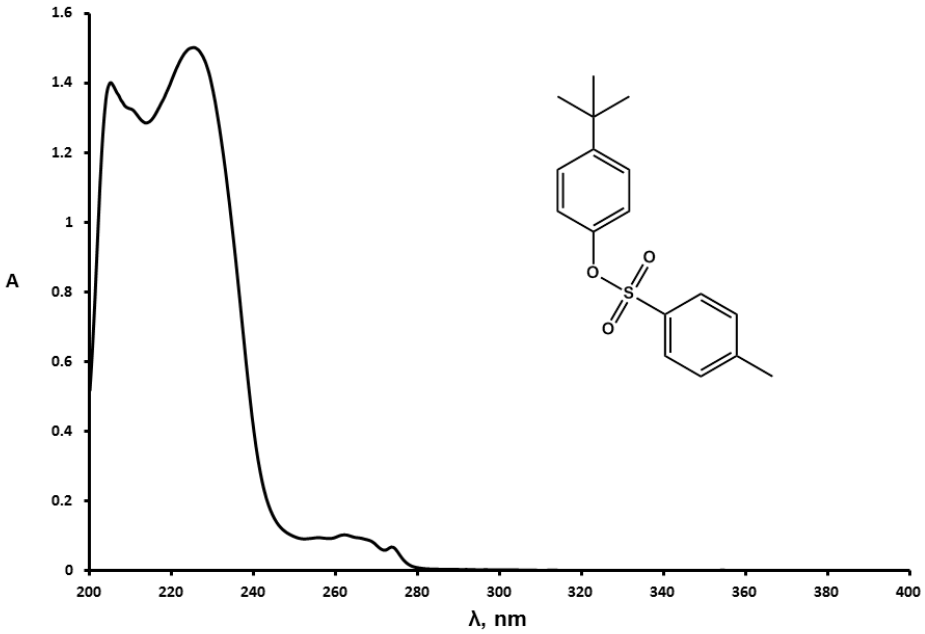


Figure S3. UV-vis spectrum of **1c** (5×10^{-5} M) in MeOH.

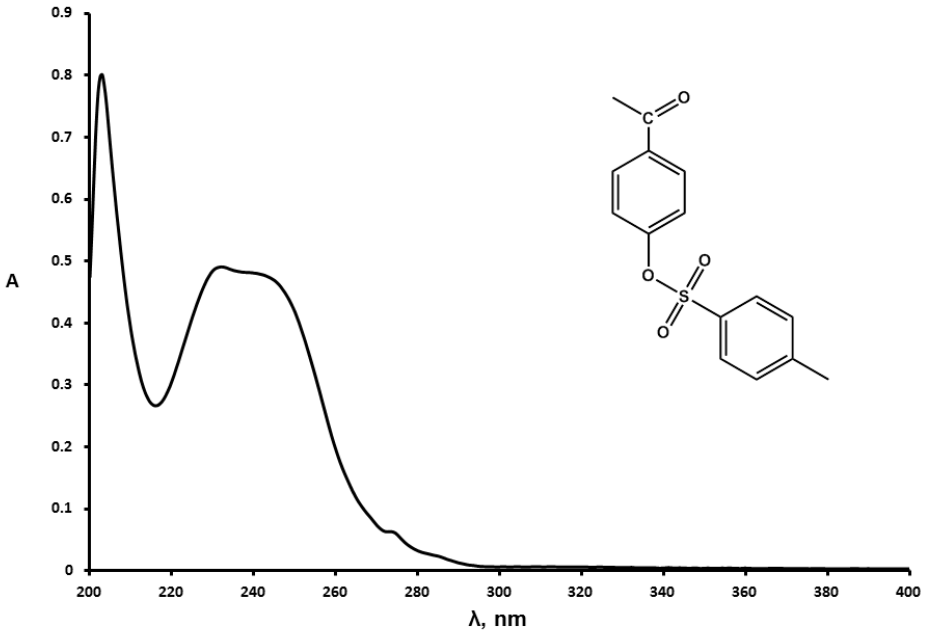


Figure S4. UV-vis spectrum of **1d** (1.25×10^{-5} M) in MeOH

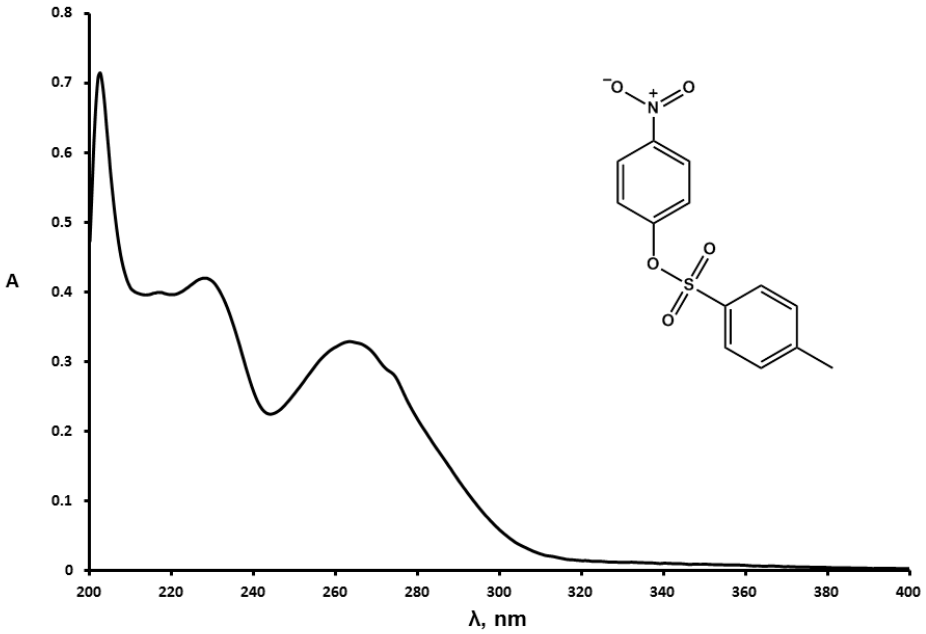


Figure S5 UV-vis spectrum of **1e** (1.25×10^{-5} M) in MeOH.

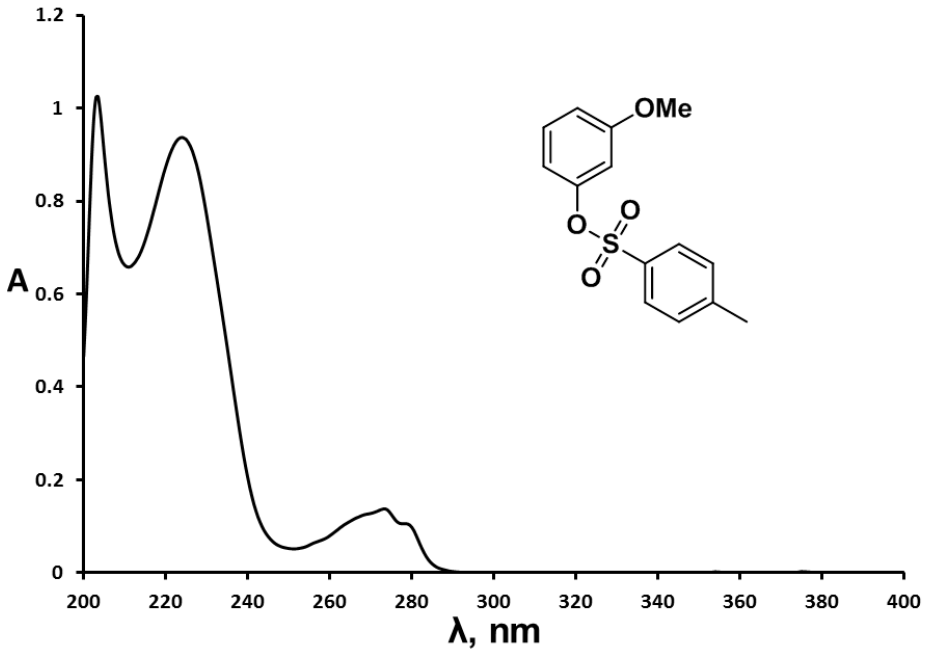


Figure S6 UV-vis spectrum of **1f** (2.5×10^{-5} M) in MeOH.

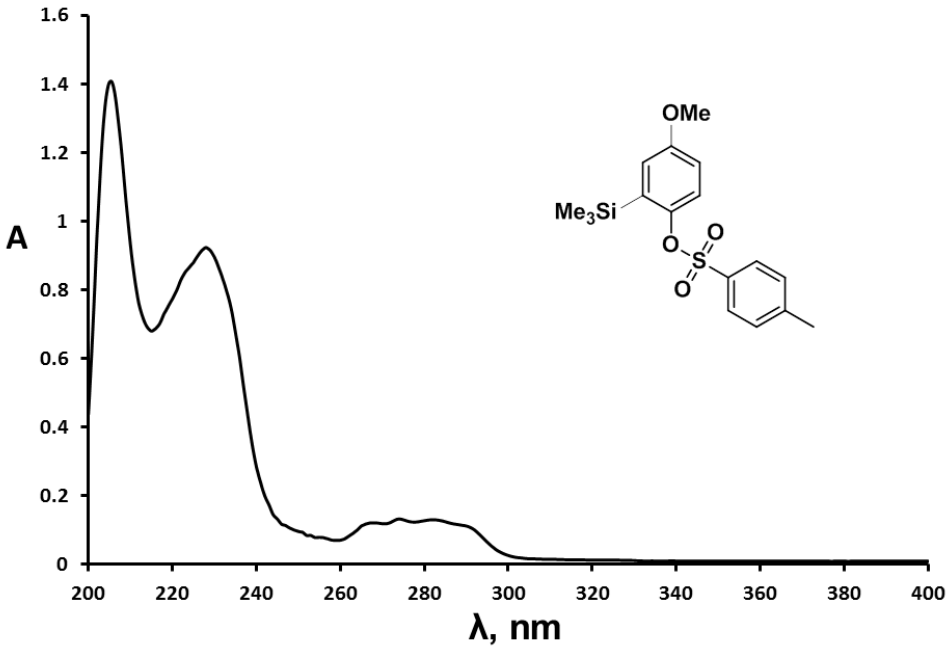


Figure S7 UV-vis spectrum of **1g** (3.2×10^{-5} M) in MeOH.

2. Potentiometric titrations of a 10^{-2} M solution of compounds 1a-d, 1f-g after irradiation (t_{irr} = 2 h) in MeOH.

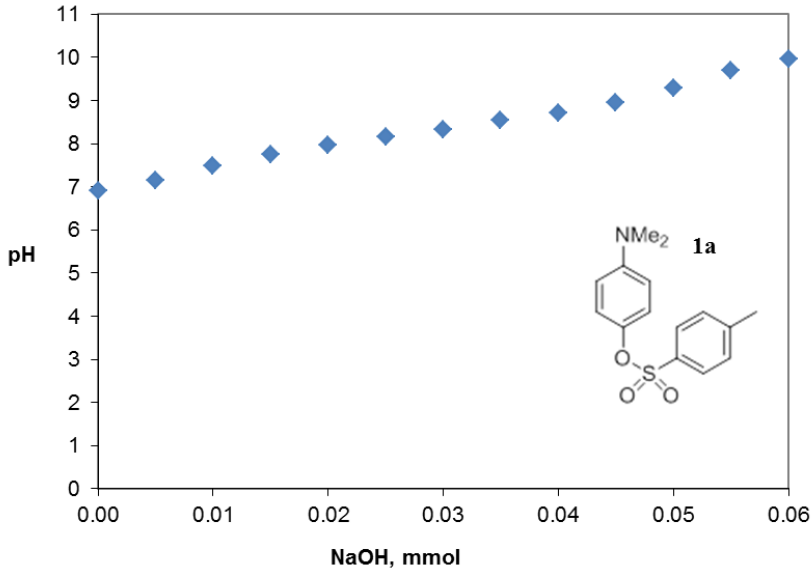


Figure S8 Potentiometric titration of a 10^{-2} M solution of **1a** after irradiation in N_2-saturated MeOH.

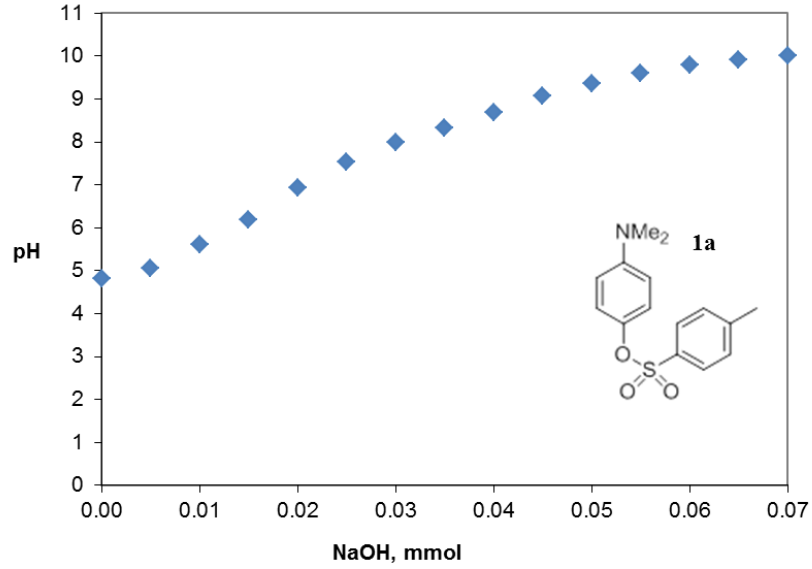


Figure S9 Potentiometric titration of a 10^{-2} M solution of **1a** after irradiation in O_2-saturated MeOH.

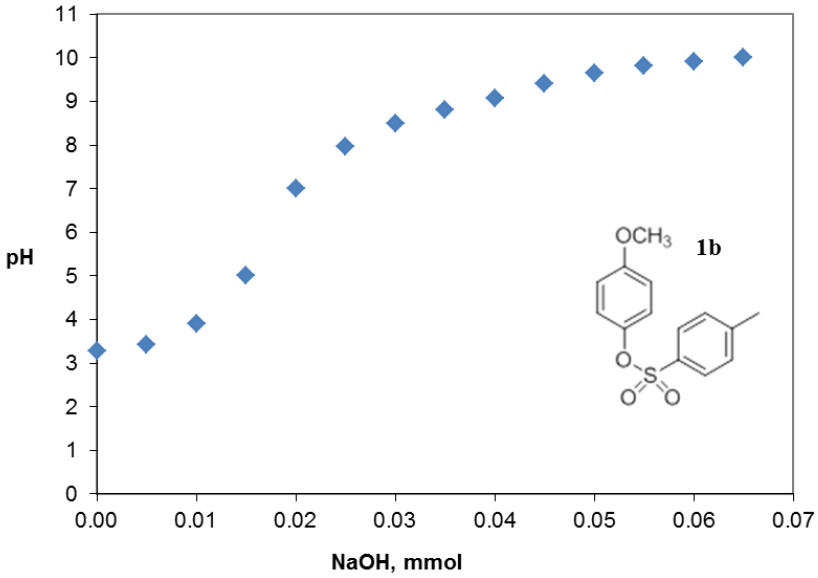


Figure S10 Potentiometric titration of a 10^{-2} M solution of **1b** after irradiation in N_2-saturated MeOH.

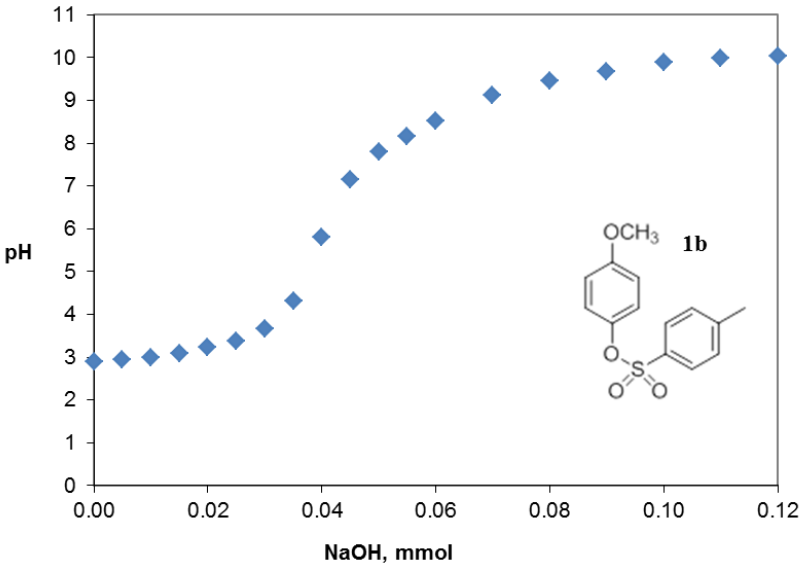


Figure S11 Potentiometric titration of a 10^{-2} M solution of **1b** after irradiation in O_2-saturated MeOH.

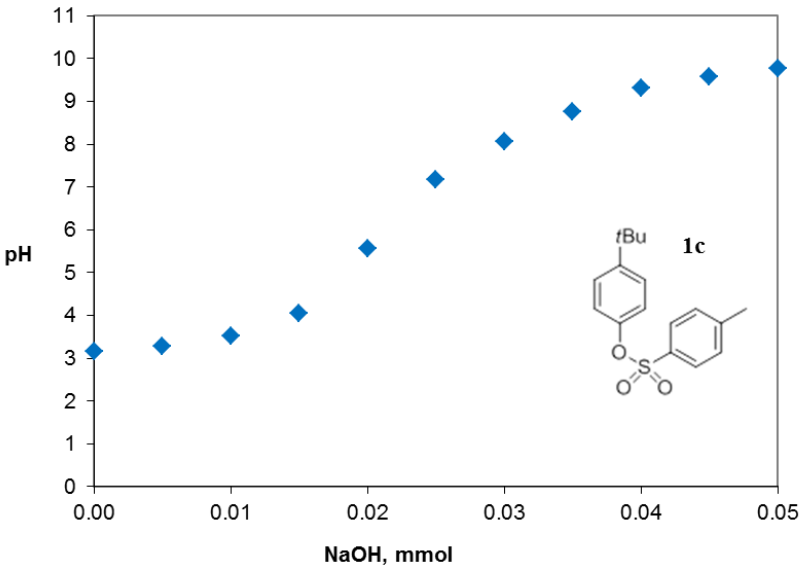


Figure S12 Potentiometric titration of a 10^{-2} M solution of **1c** after irradiation in N_2-saturated MeOH.

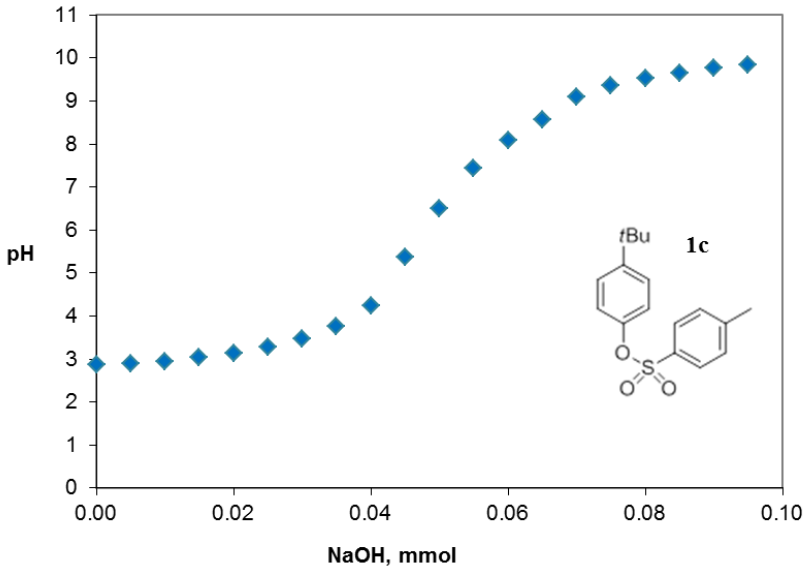


Figure S13 Potentiometric titration of a 10^{-2} M solution of **1c** after irradiation in O_2-saturated MeOH.

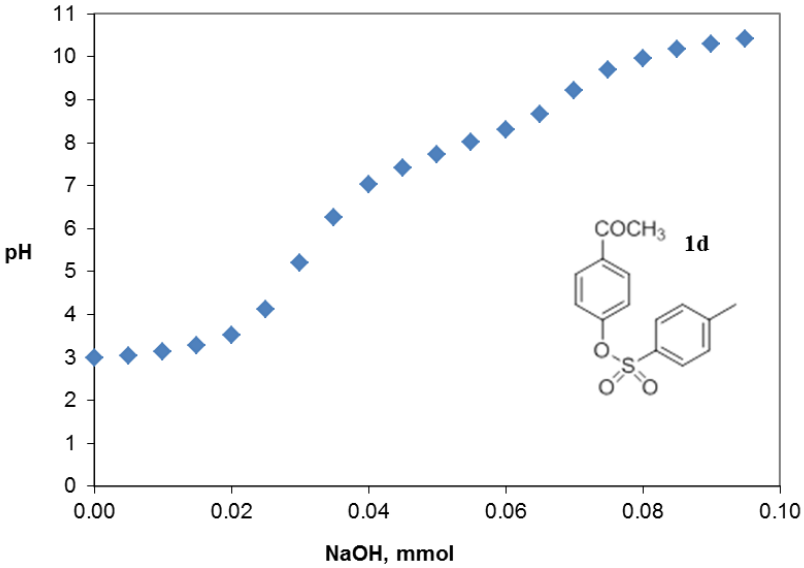


Figure S14 Potentiometric titration of a 10^{-2} M solution of **1d** after irradiation in N_2-saturated MeOH.

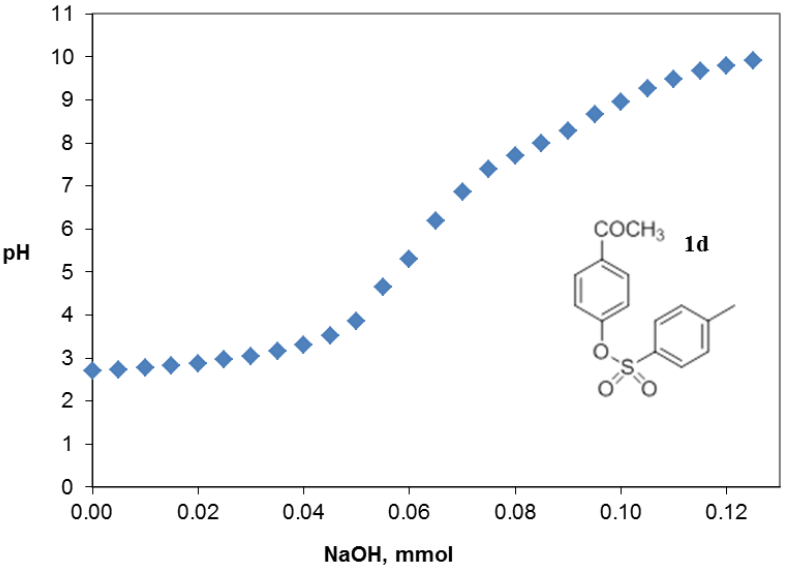


Figure S15 Potentiometric titration of a 10^{-2} M solution of **1d** after irradiation in O_2-saturated MeOH.

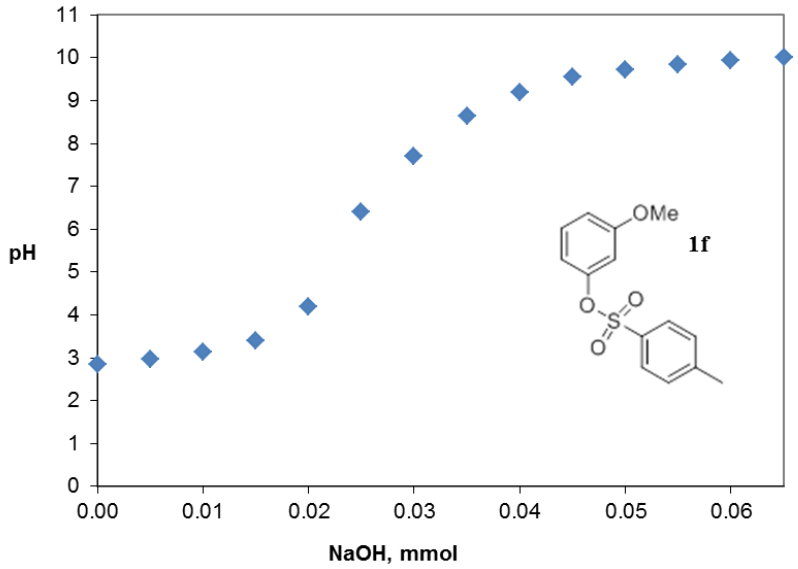


Figure S16 Potentiometric titration of a 10^{-2} M solution of **1f** after irradiation in N_2-saturated MeOH.

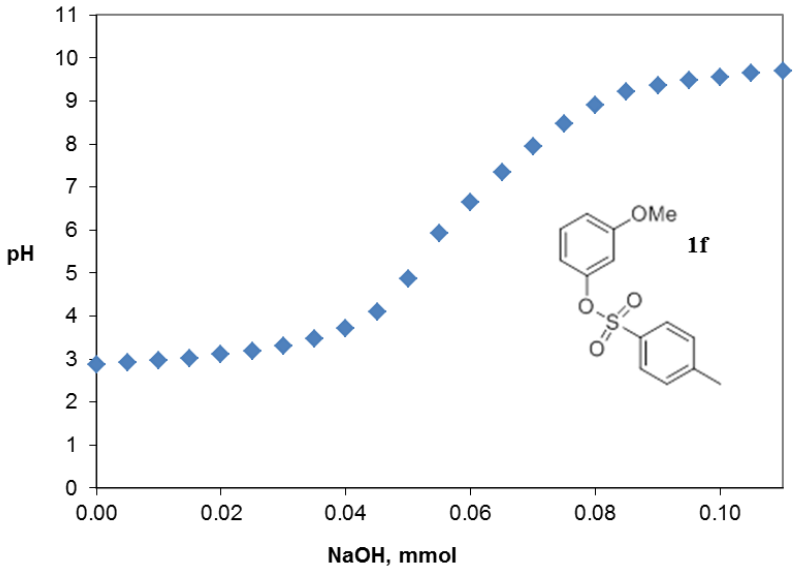


Figure S17 Potentiometric titration of a 10^{-2} M solution of **1f** after irradiation in O_2-saturated MeOH.

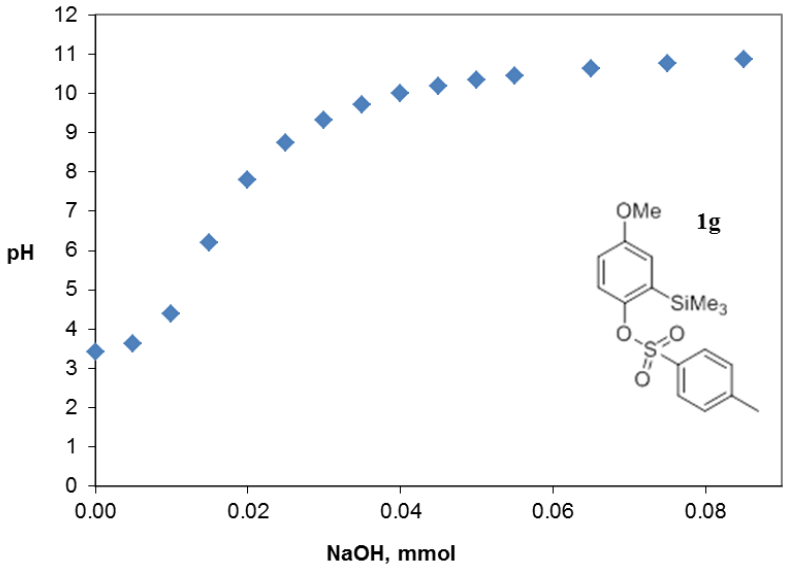


Figure S18 Potentiometric titration of a 10^{-2} M solution of **1g** after irradiation in N_2-saturated MeOH.

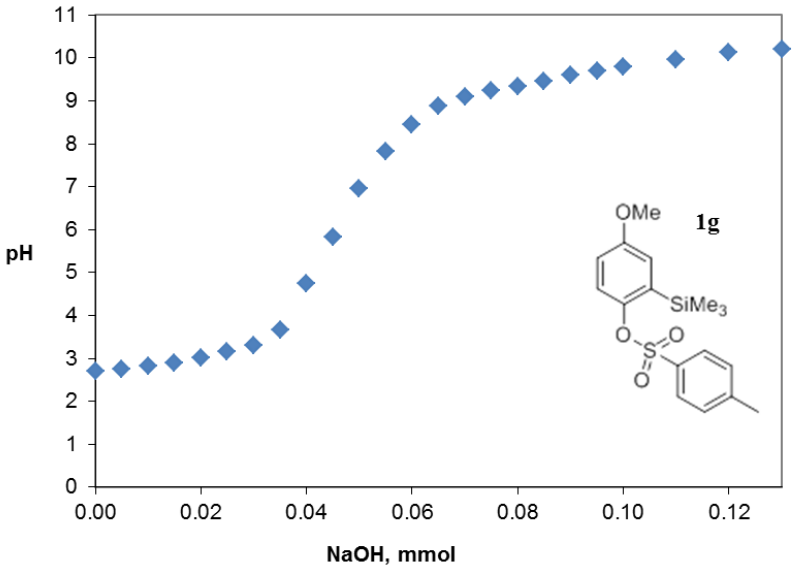


Figure S19 Potentiometric titration of a 10^{-2} M solution of **1g** after irradiation in O_2-saturated MeOH.

3. Irradiation and LFP experiments on 1b and 1d

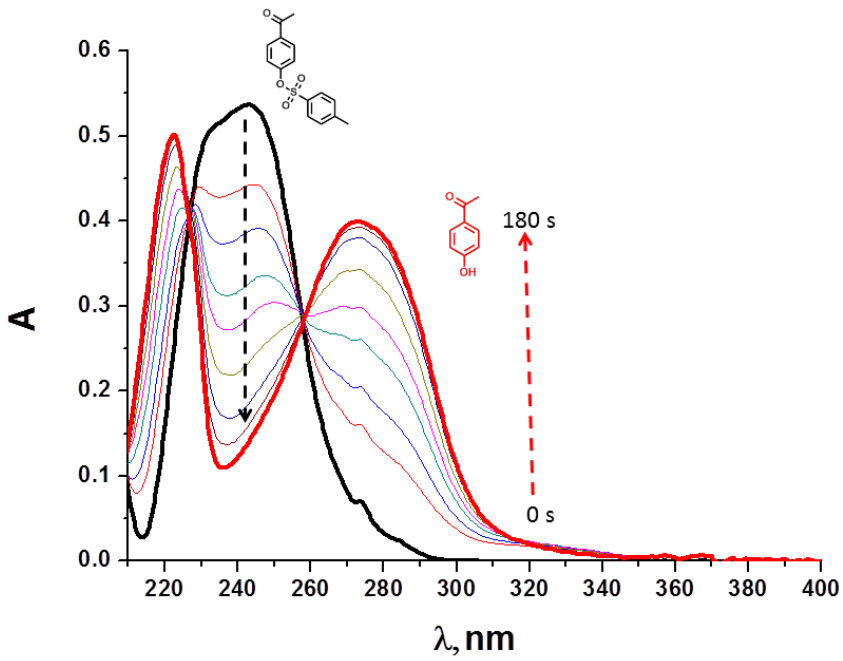


Figure S20 Absorption spectra of **1d** (2.9×10^{-5} M) in N_2 saturated MeOH during irradiation (1×15 W Hg lamp, λ_{em} = 254 nm).

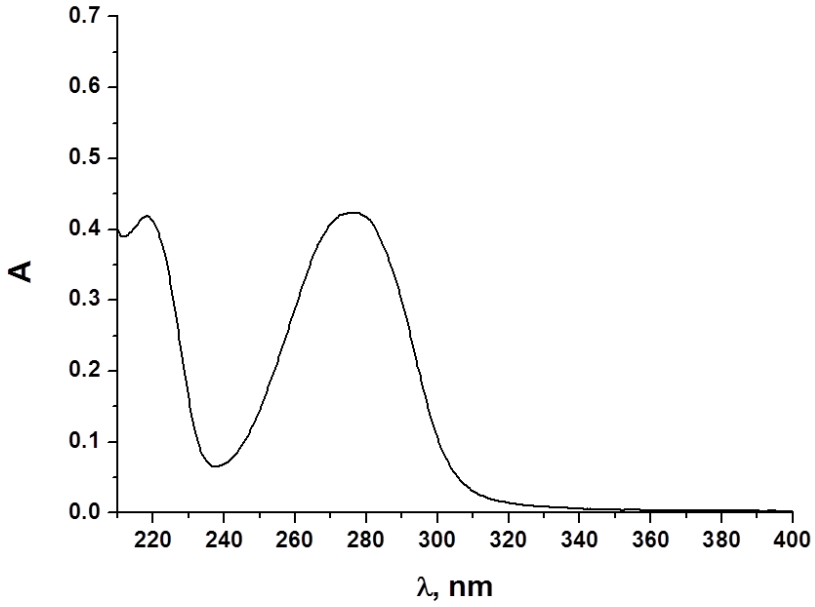


Figure S21 UV-vis spectrum of **2d** (2.6×10^{-5} M) in MeOH.

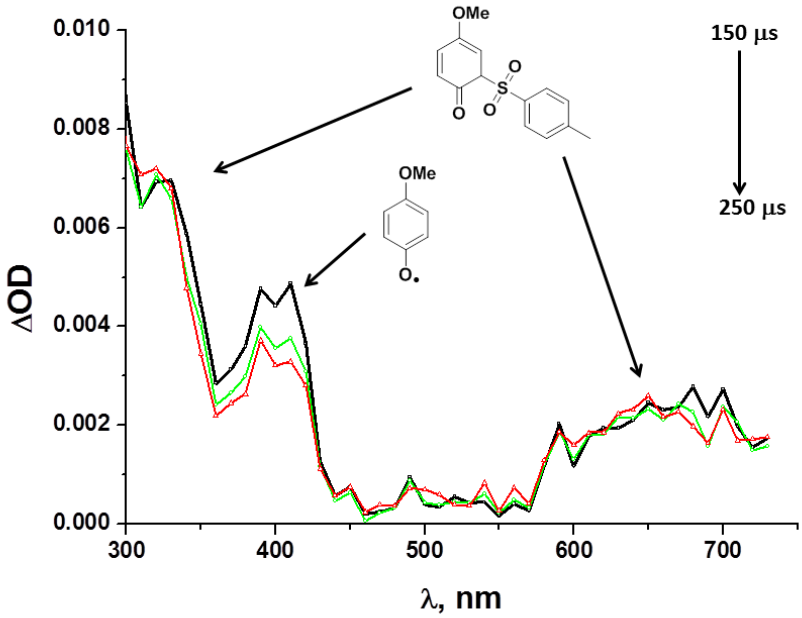
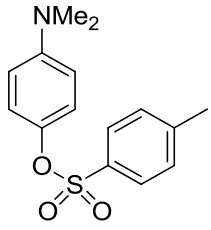
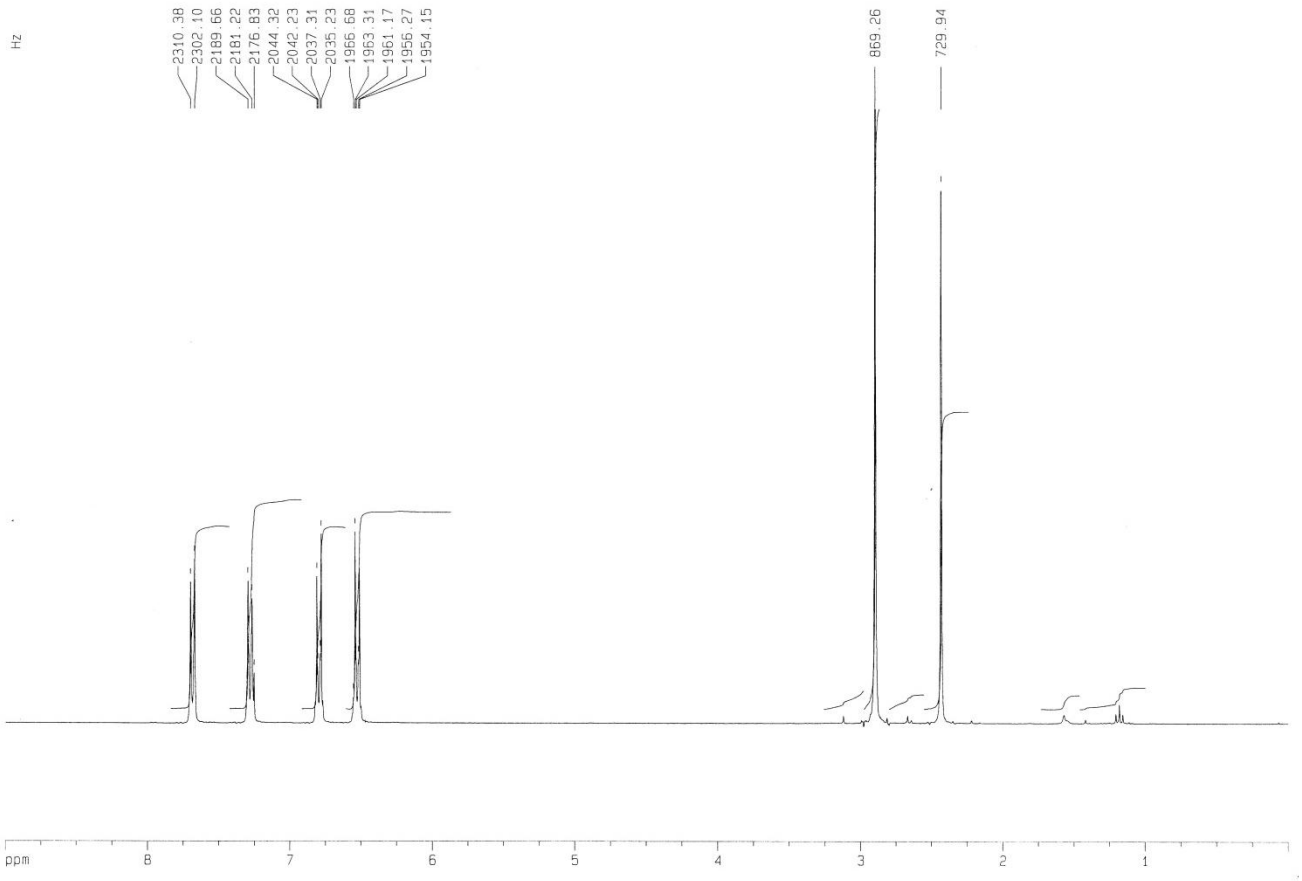


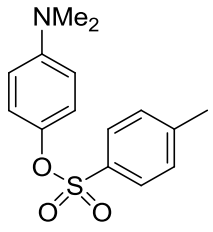
Figure S22 Transient spectra of a solution of **1b** (10^{-4} M) in Argon saturated methanol recorded 150 µs after a 20 ns laser pulse (λ = 266 nm).

4. ^{1}H and ^{13}C spectra of compounds 1a-g and 3a, 3b, 3g.

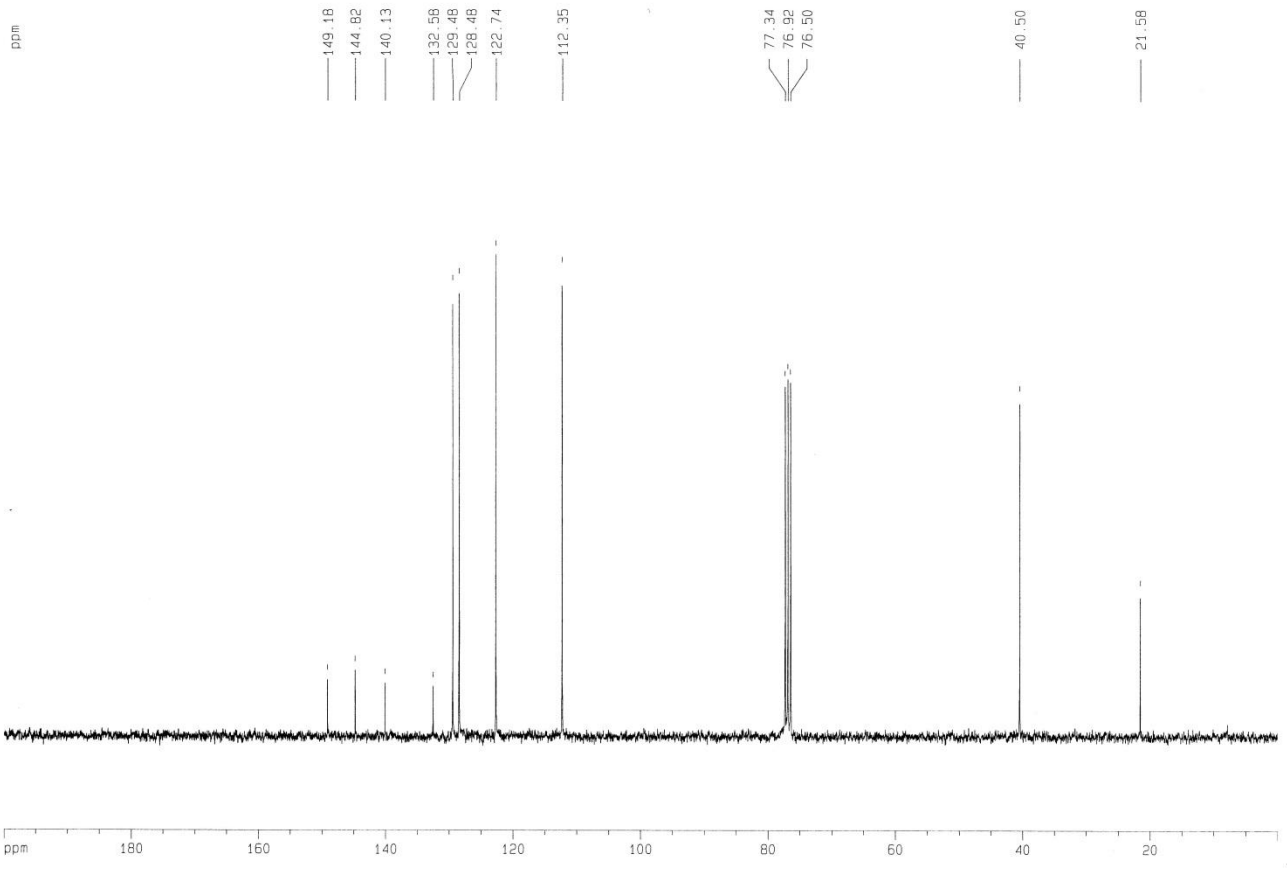


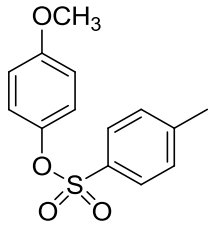
1a, ^{1}H NMR (δ, $CDCl_3$).



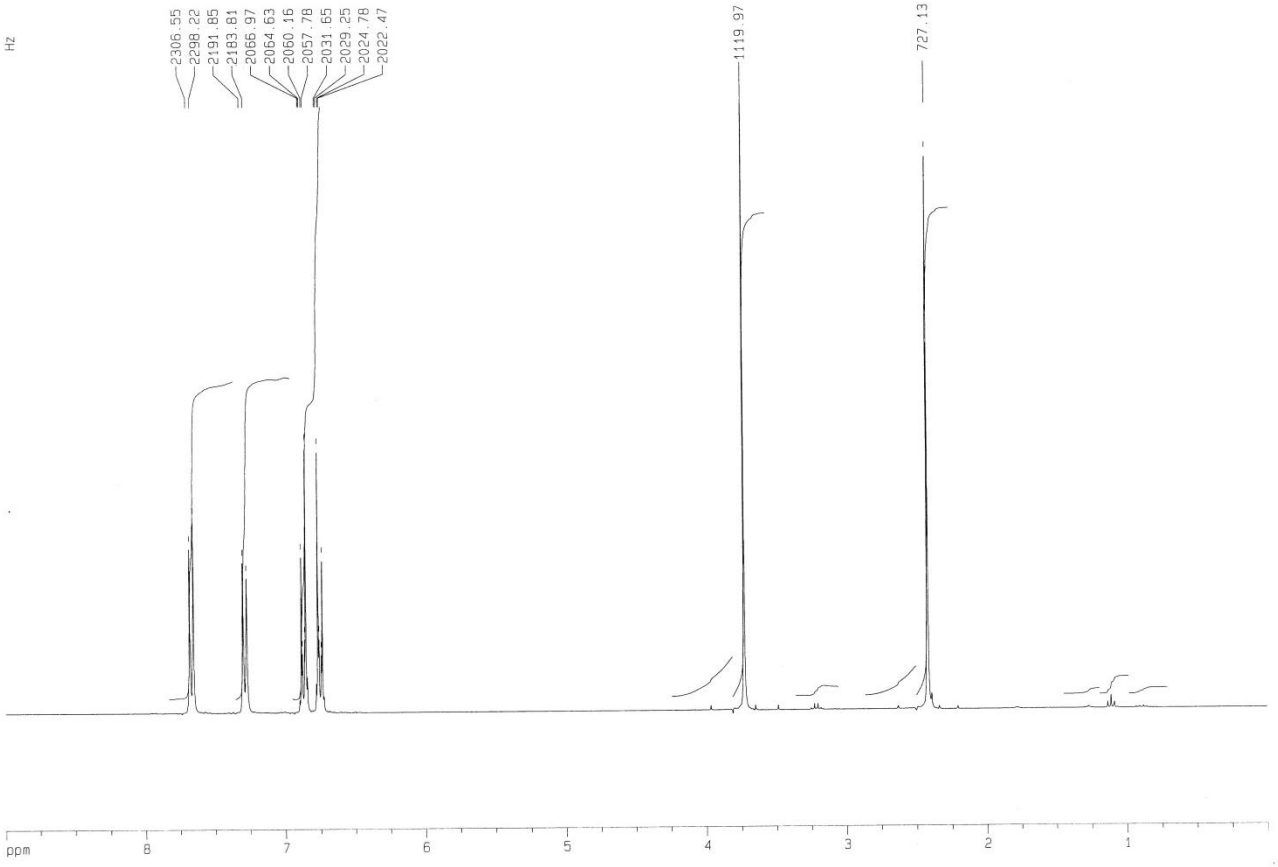


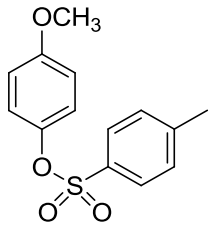
1a, ^{13}C NMR (δ, $CDCl_3$).



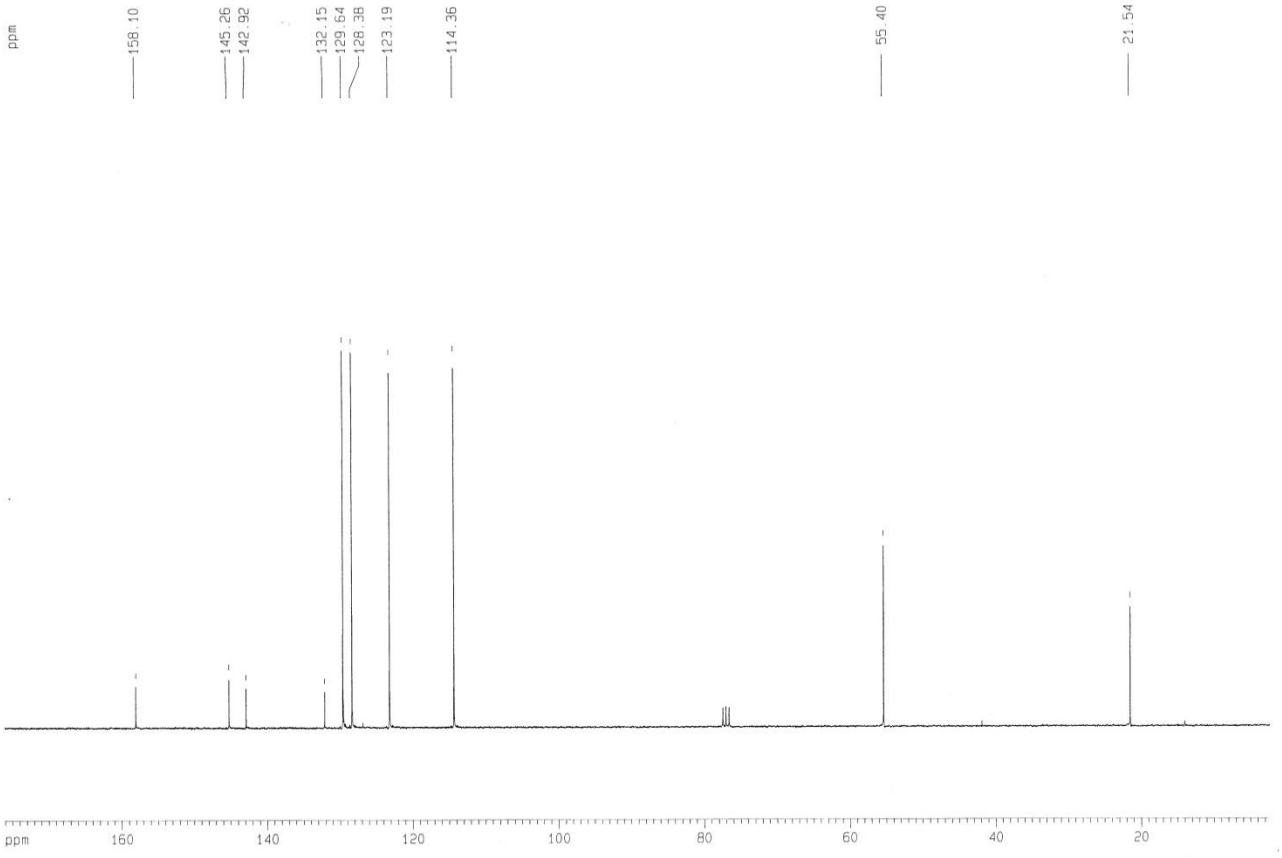


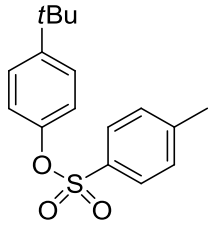
1b, ^{1}H NMR (δ, $CDCl_3$).



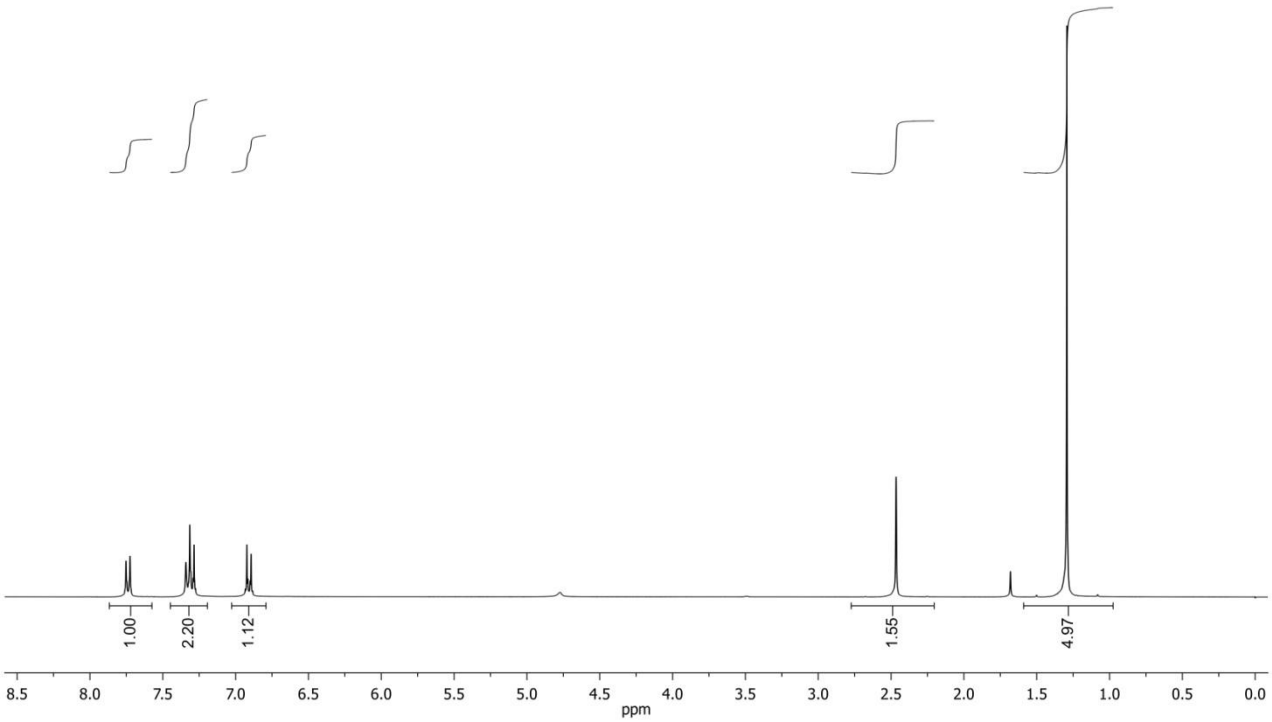


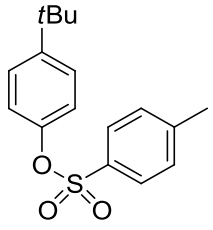
1b, ^{13}C NMR (δ, $CDCl_3$).



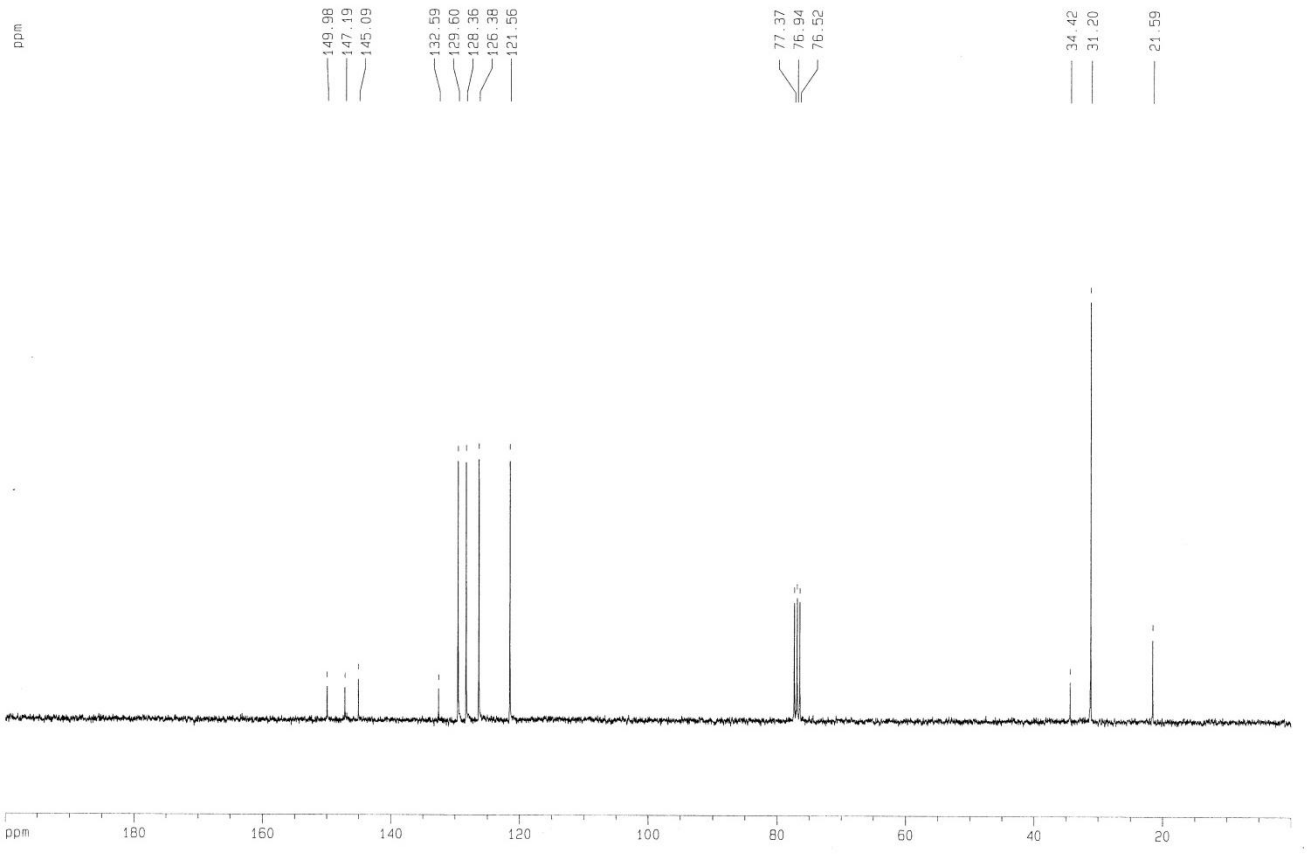


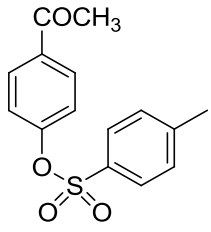
1c, ^{1}H NMR (δ, $CDCl_3$).



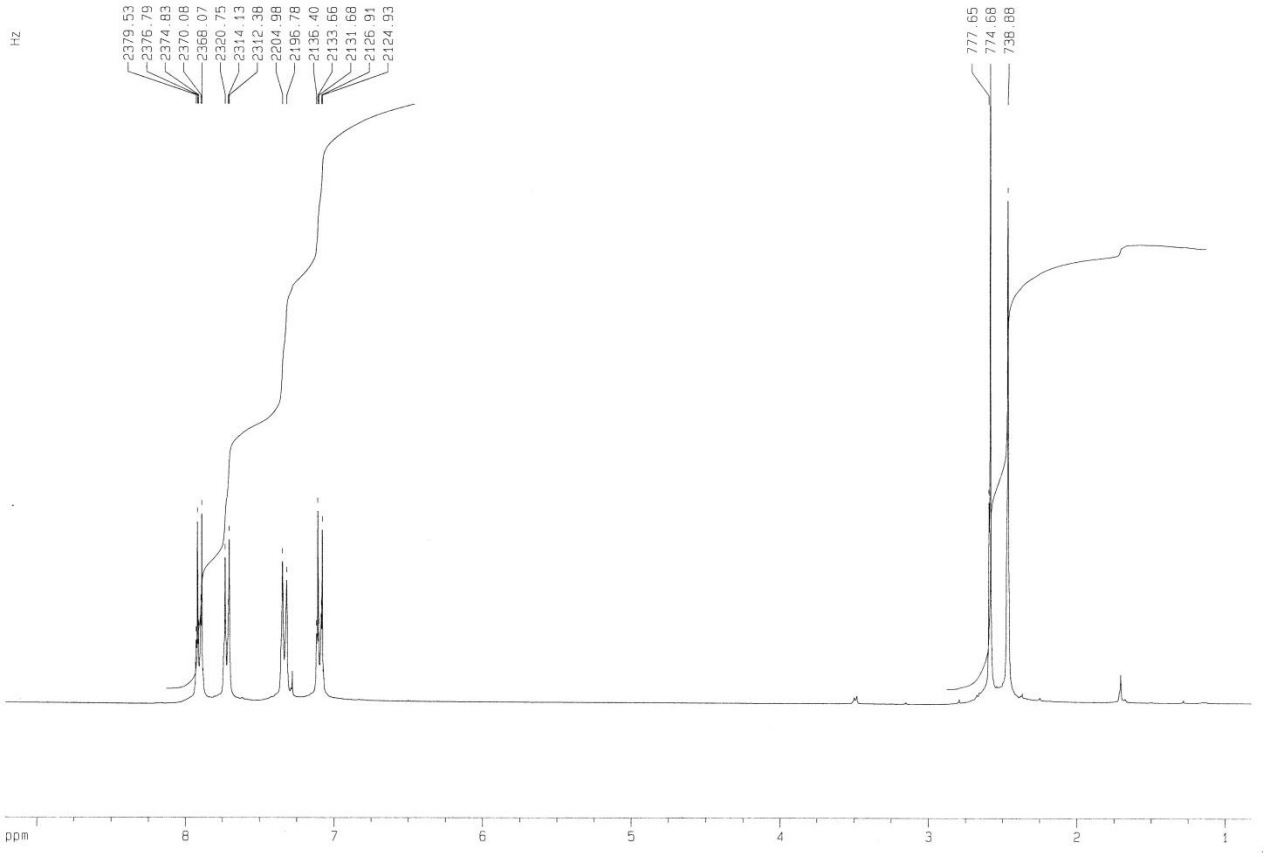


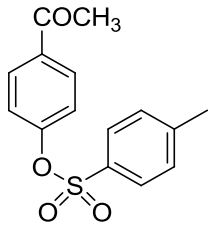
1c, ^{13}C NMR (δ, $CDCl_3$).



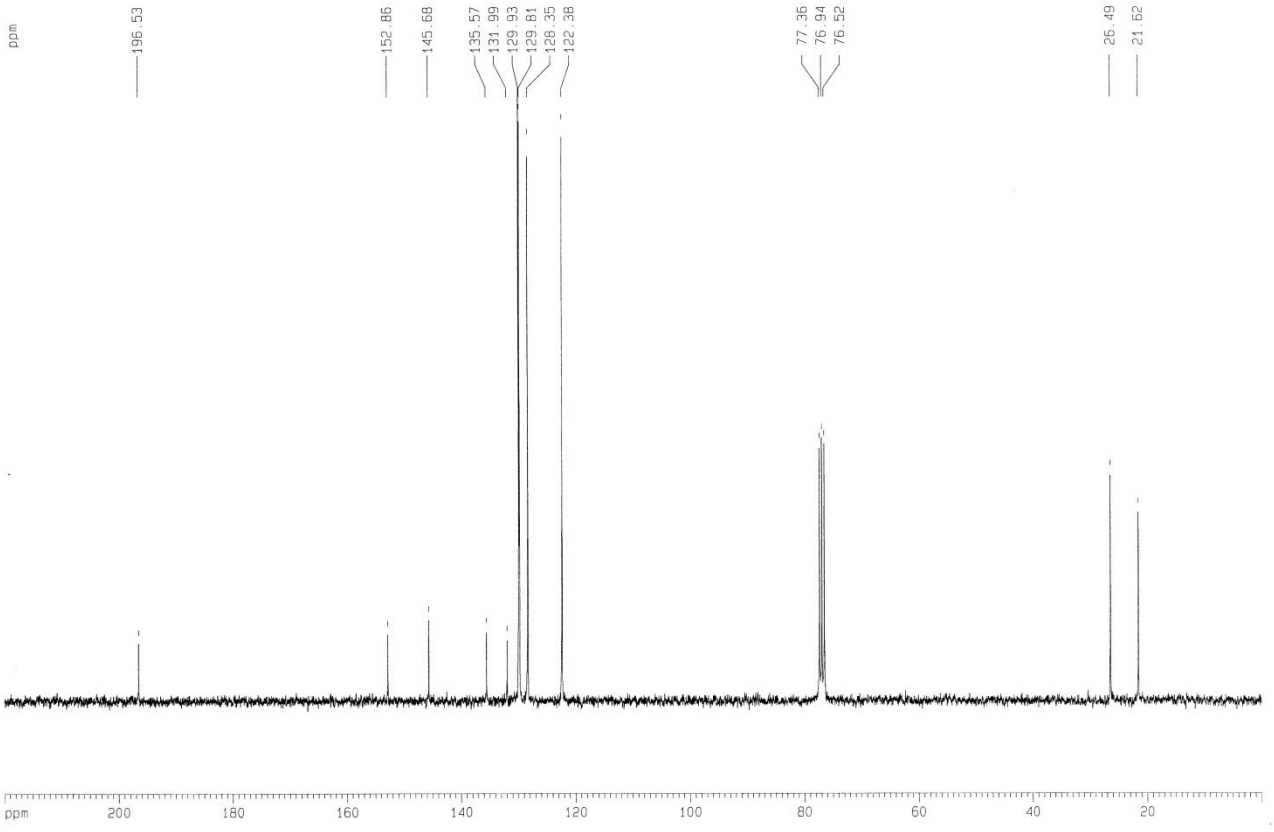


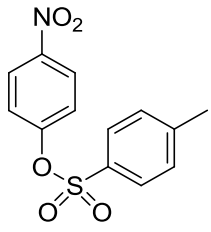
1d, ^{1}H NMR (δ, $CDCl_3$).



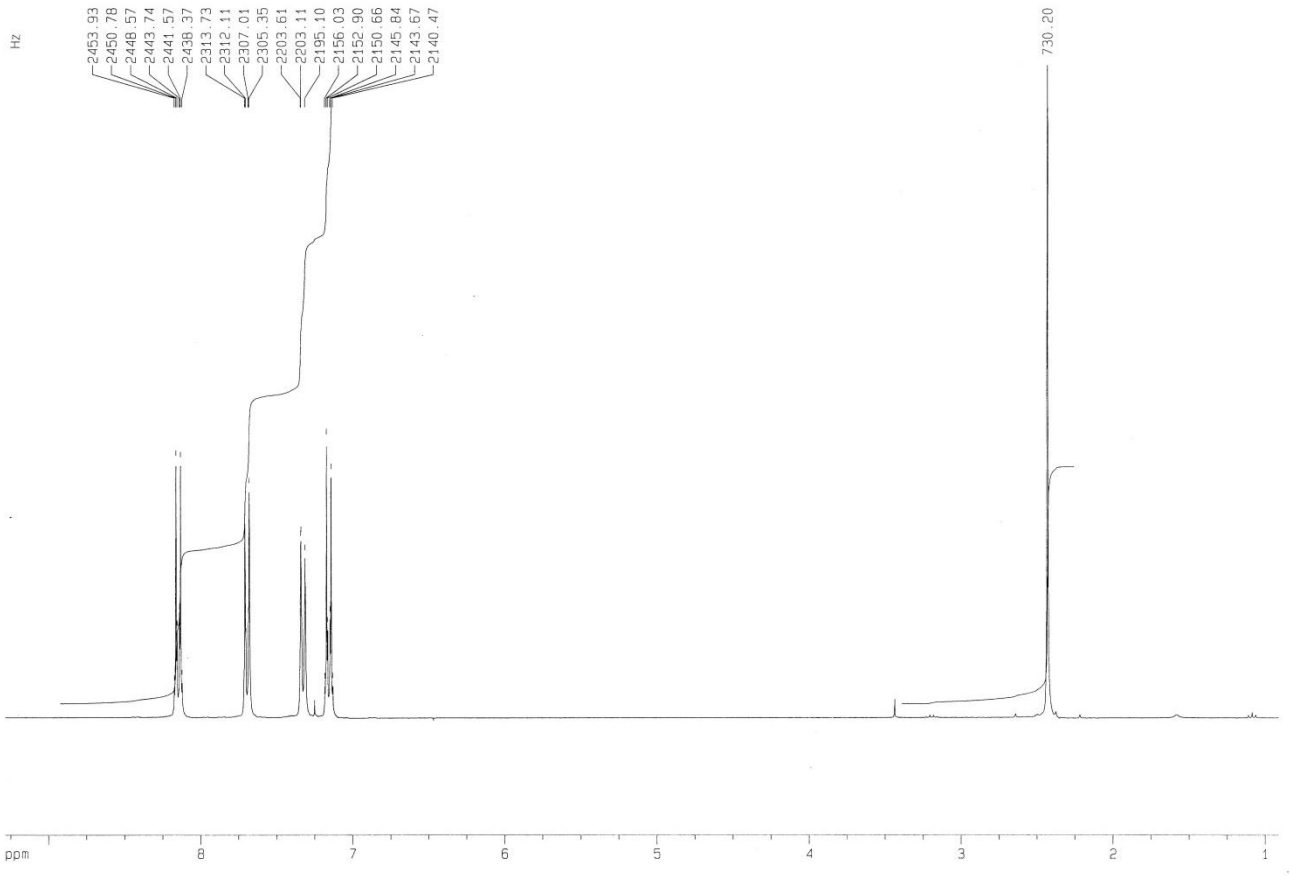


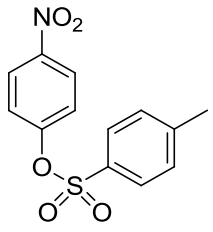
1d, ^{13}C NMR (δ, $CDCl_3$).



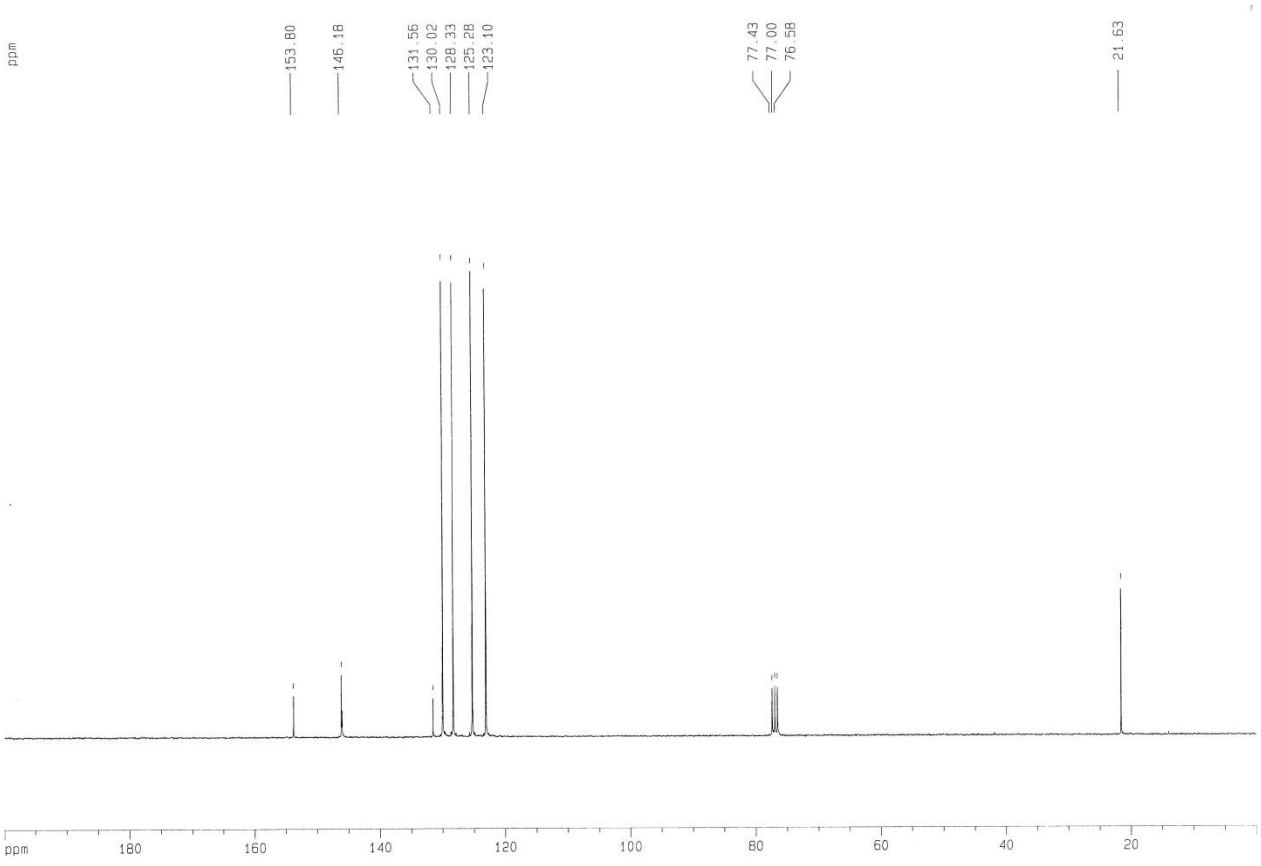


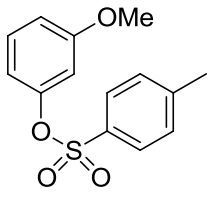
1e, ^{1}H NMR (δ, $CDCl_3$).



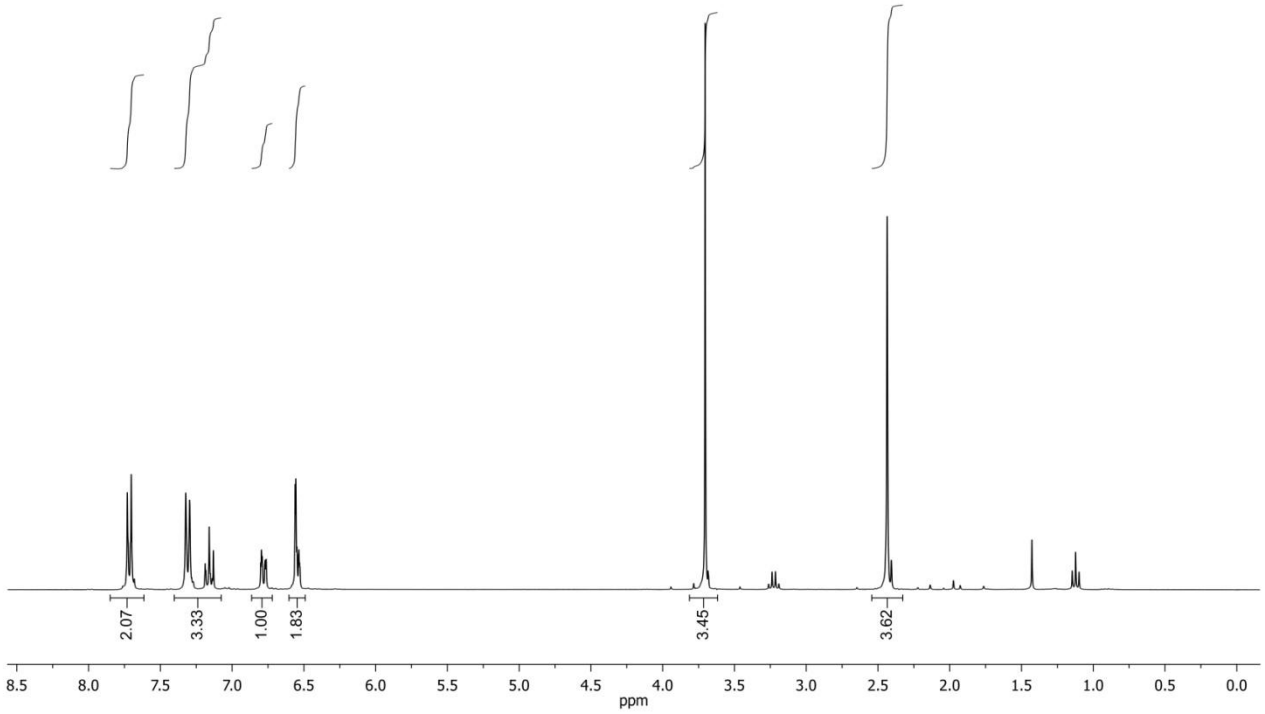


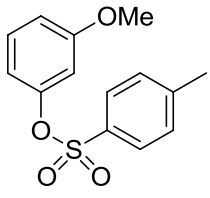
1e, ^{13}C NMR (δ, $CDCl_3$).



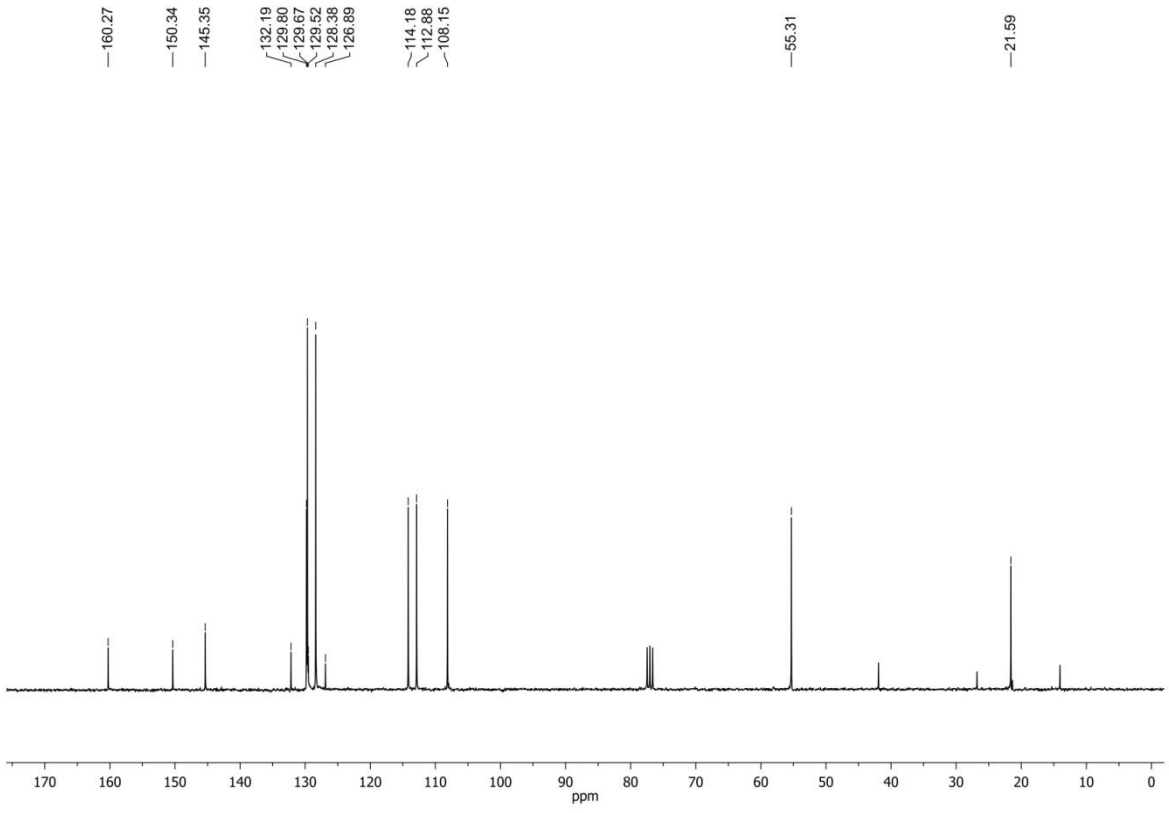


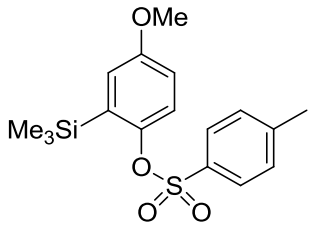
1f, ^{1}H NMR (δ, $CDCl_3$).



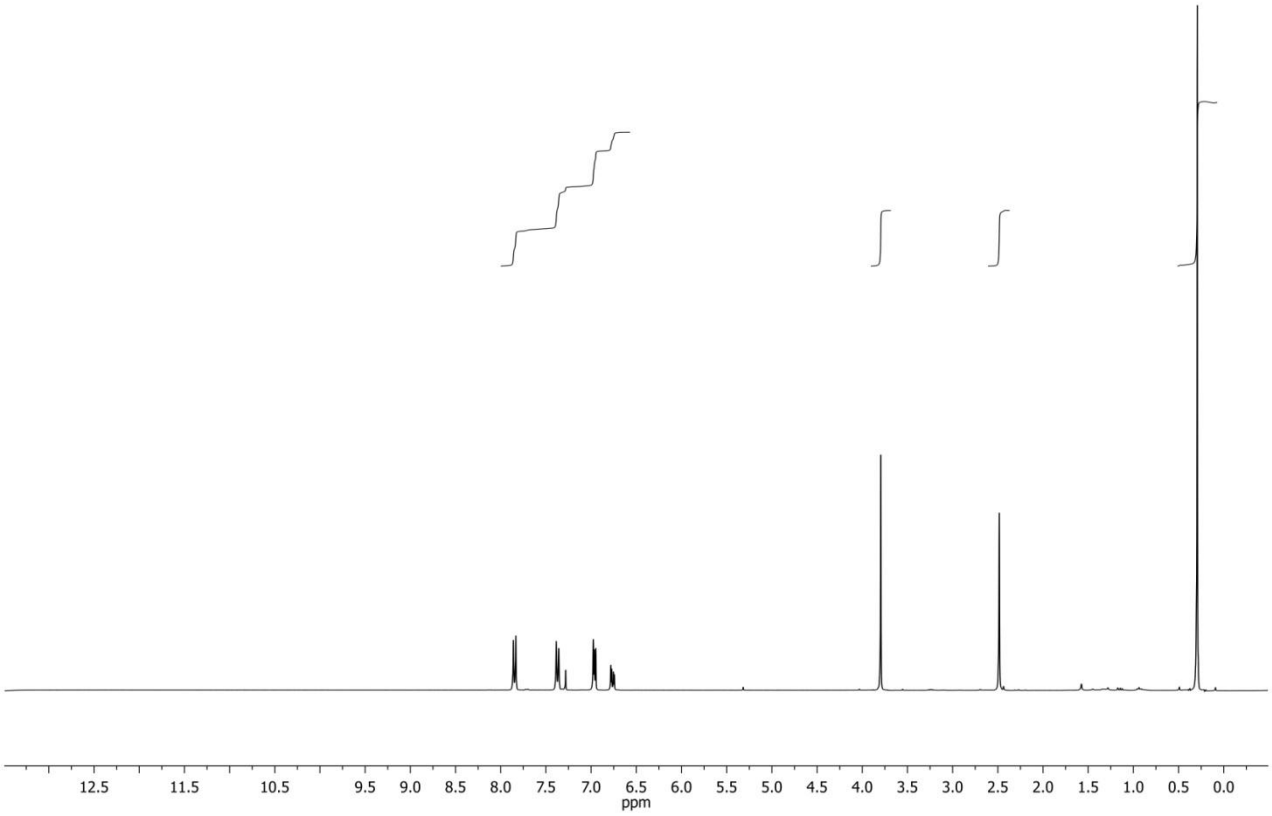


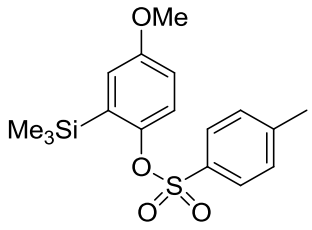
1f, ^{13}C NMR (δ, $CDCl_3$).



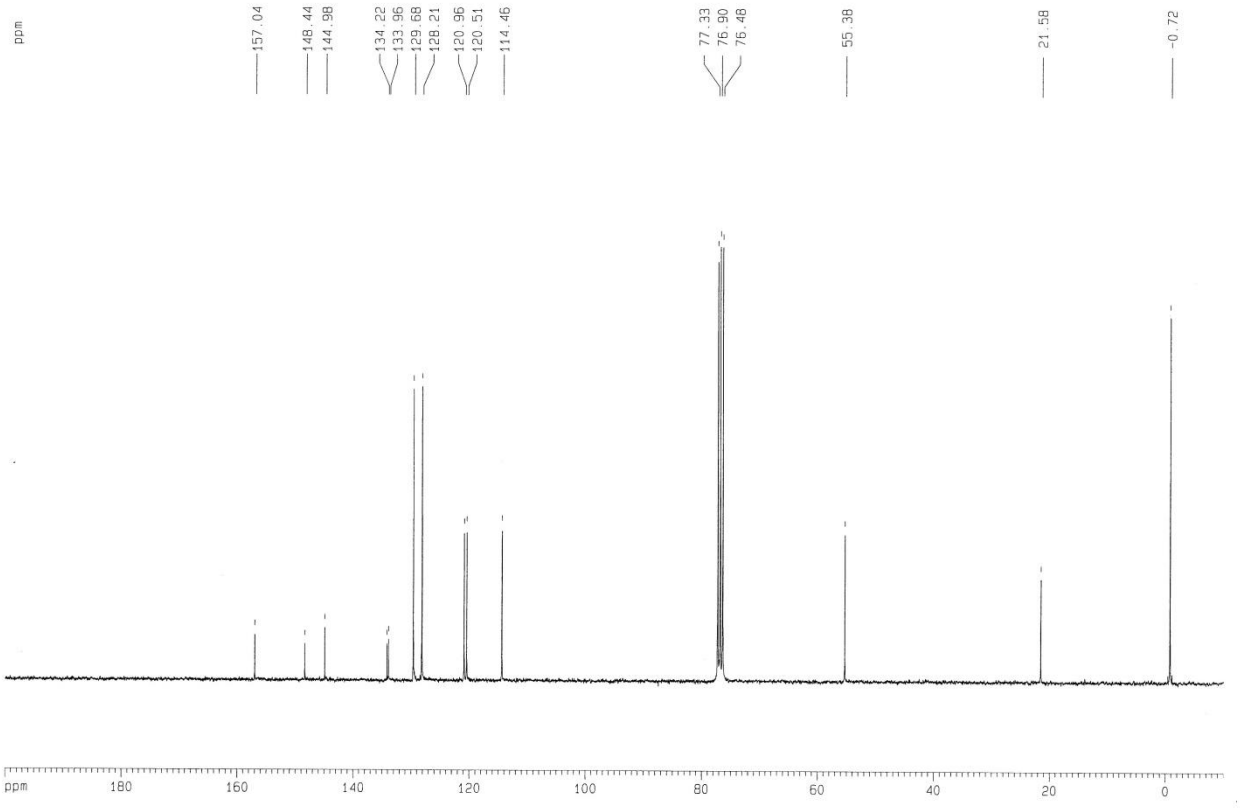


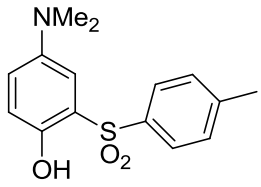
1g, ^{1}H NMR (δ, $CDCl_3$).



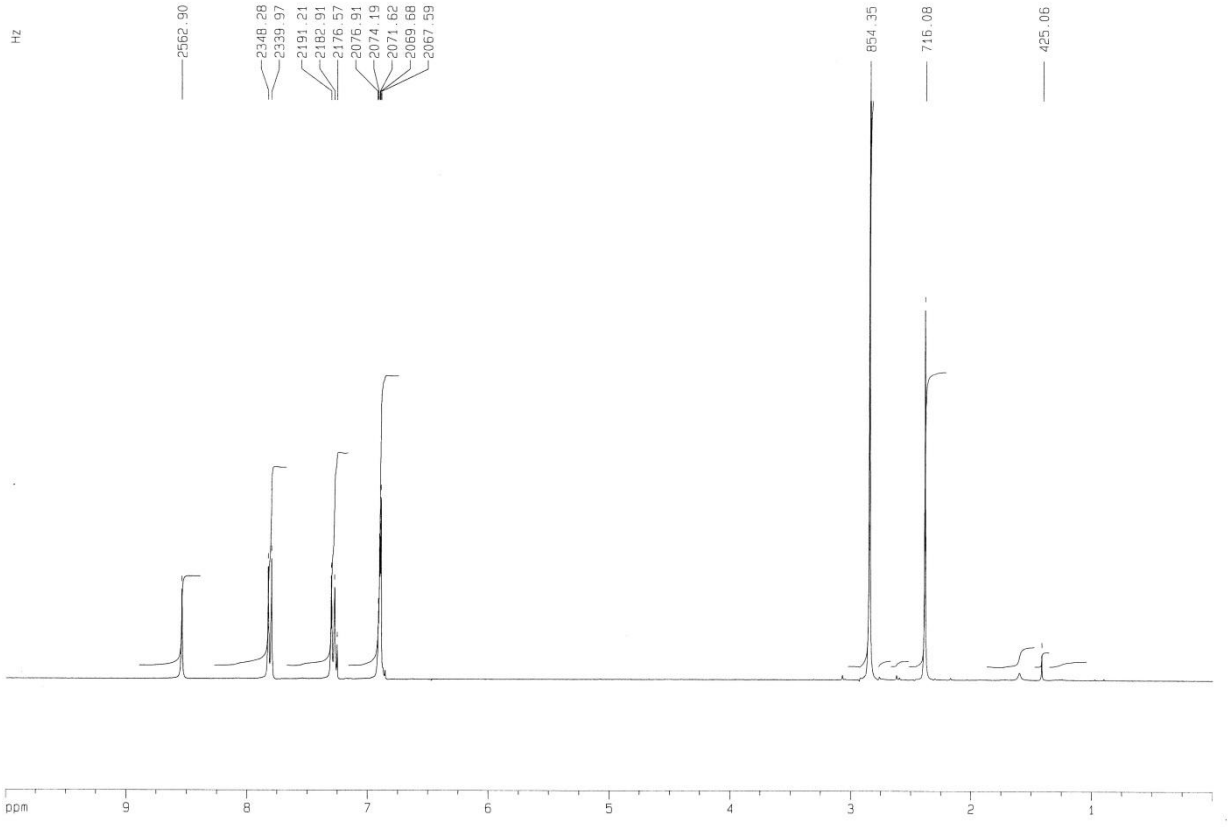


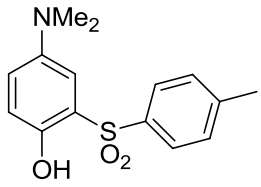
1g, ^{13}C NMR (δ, $CDCl_3$).



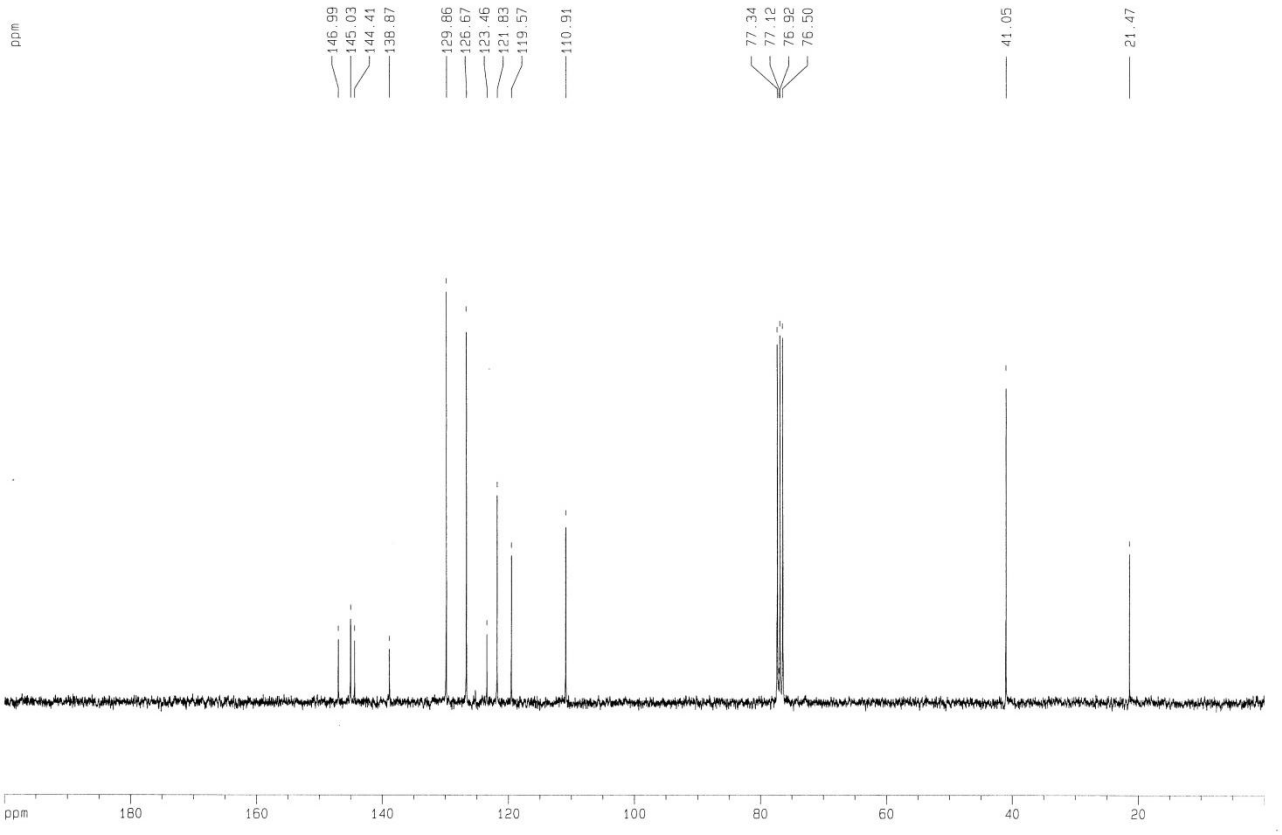


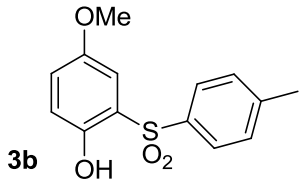
3a, ^{1}H NMR (δ, $CDCl_3$).





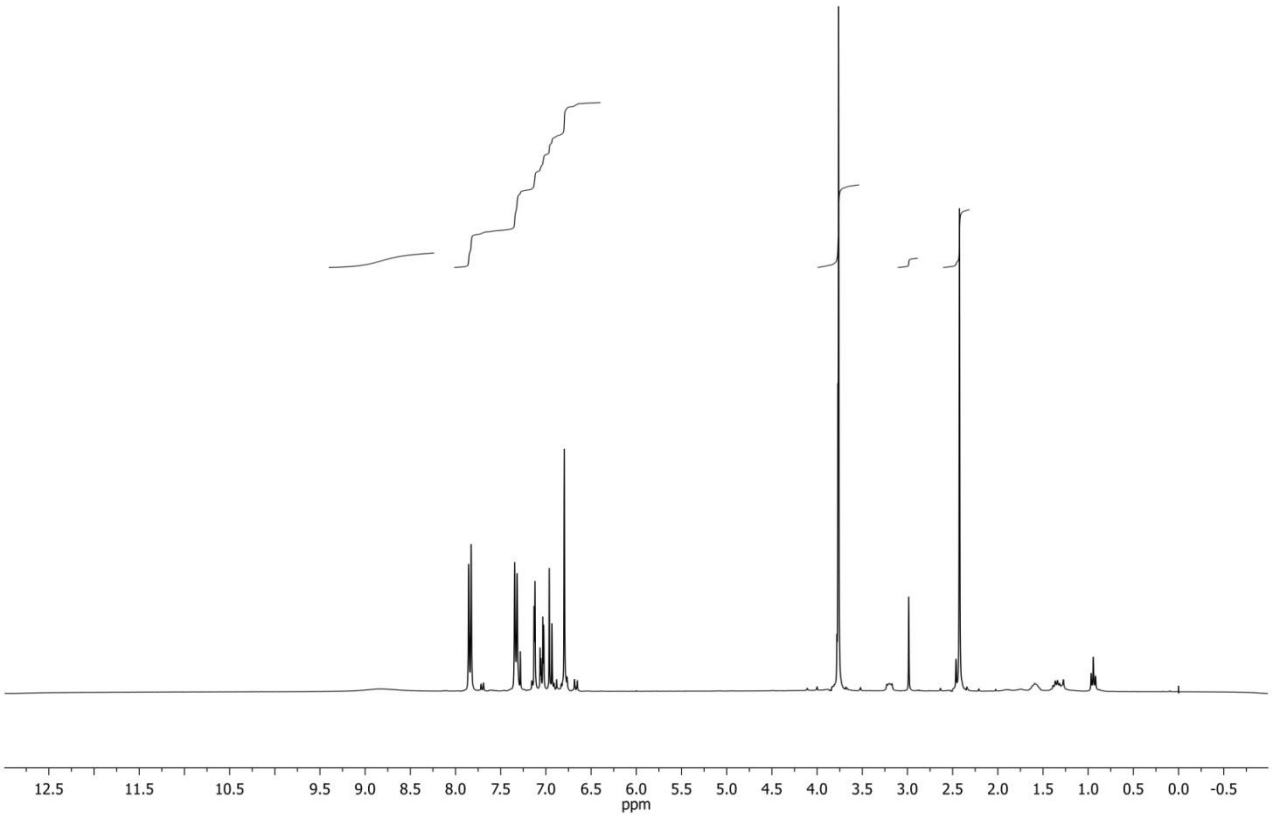
3a, ^{13}C NMR (δ, $CDCl_3$).

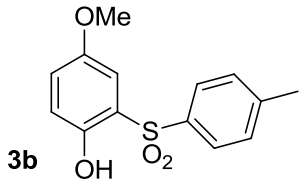




3b + **1b**

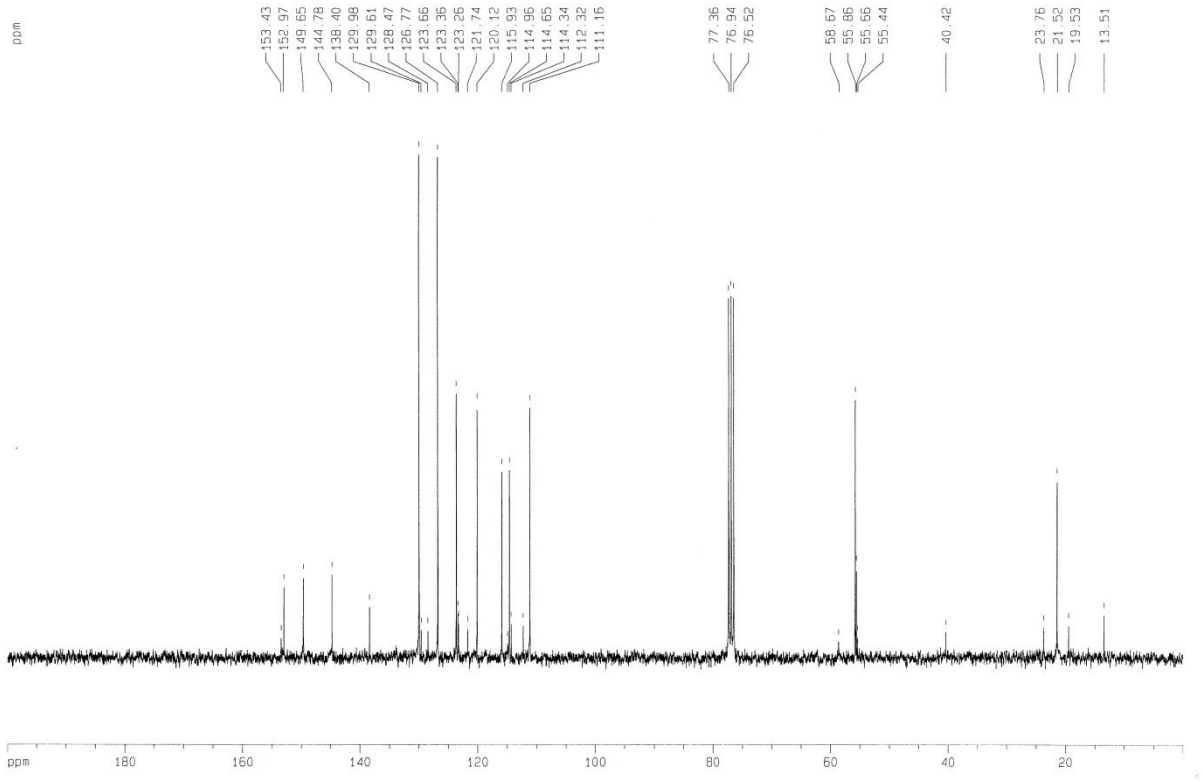
3b, ^{1}H NMR of the mixture (δ, $CDCl_3$).

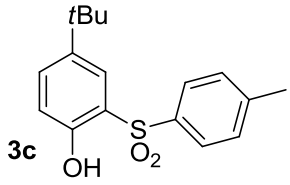




3b + **1b**

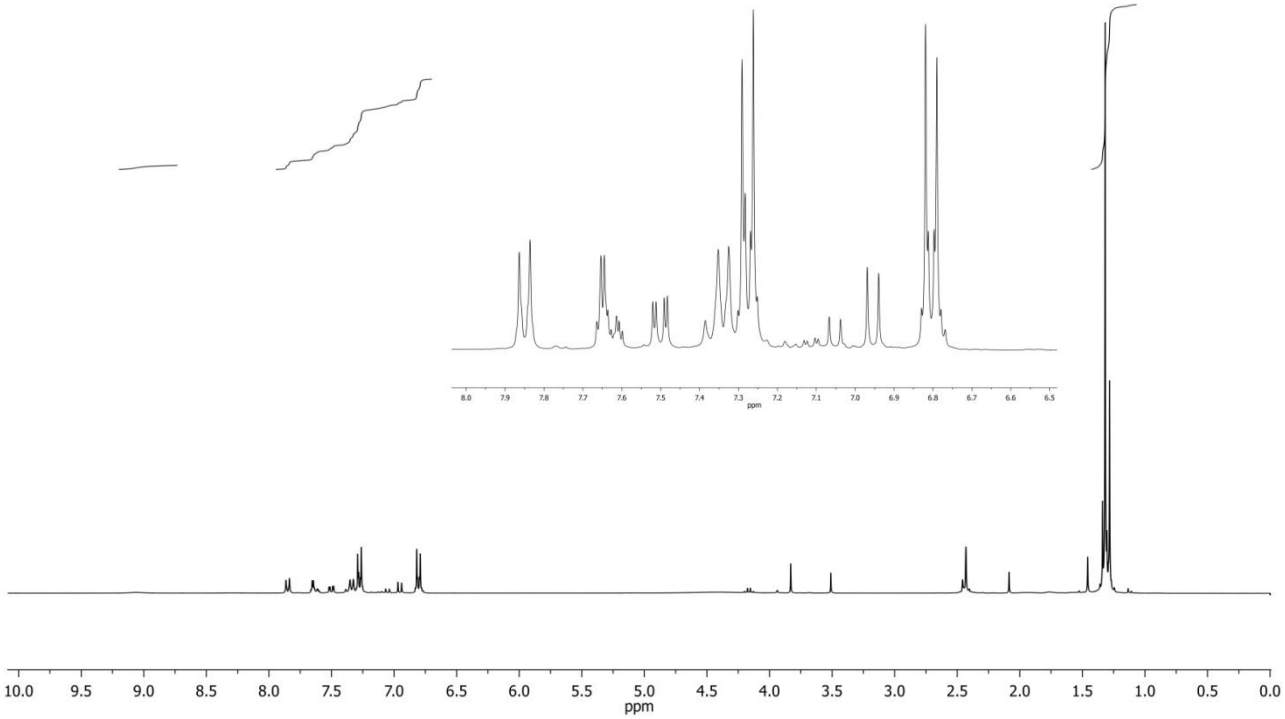
3b, ^{13}C NMR of the mixture (δ, $CDCl_3$).

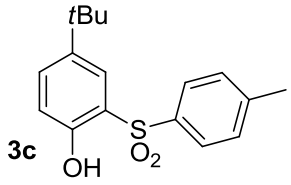




3c + **2c**

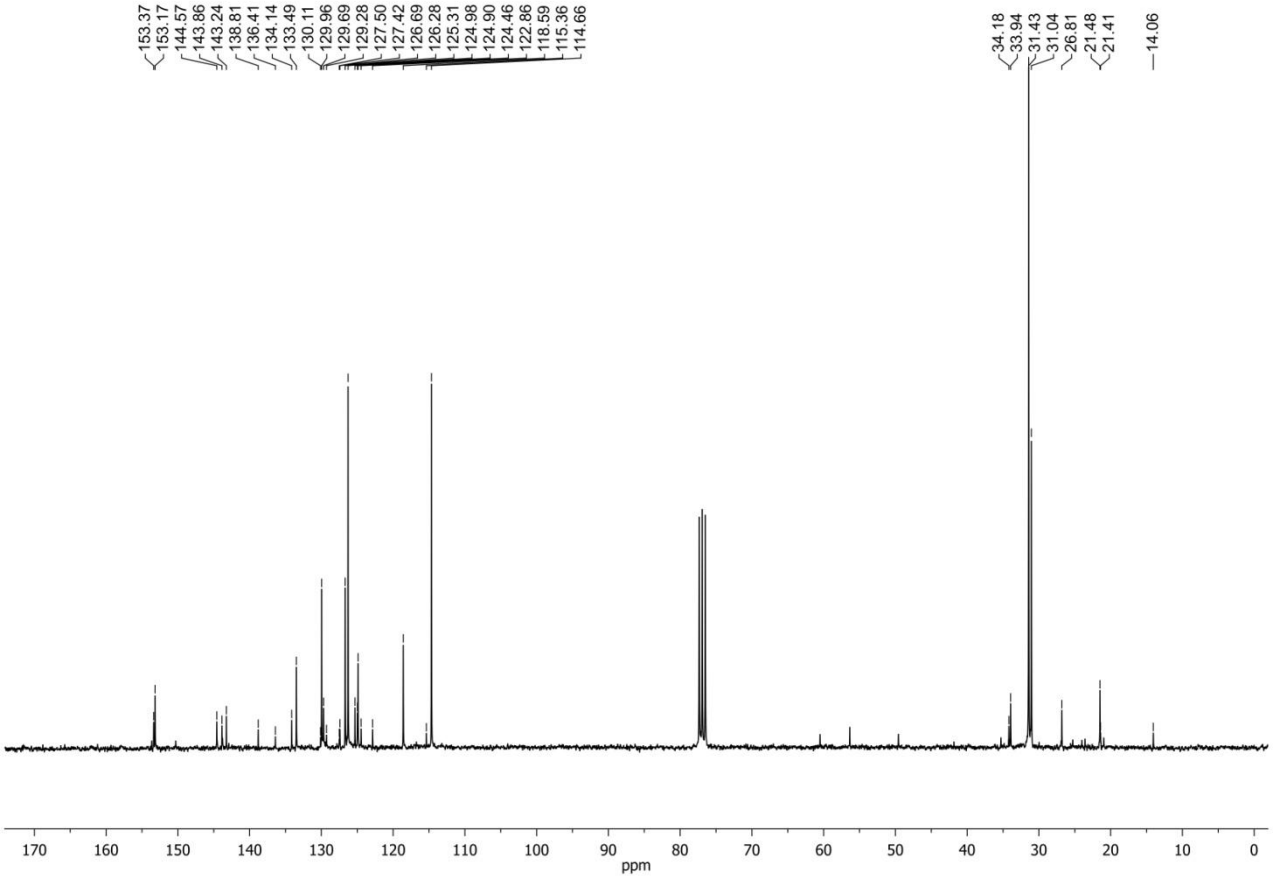
3c, ^{1}H NMR of the mixture (δ, $CDCl_3$).

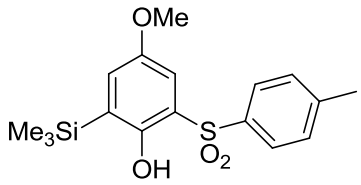




3c + **2c**

3c, ^{13}C NMR of the mixture (δ, $CDCl_3$).

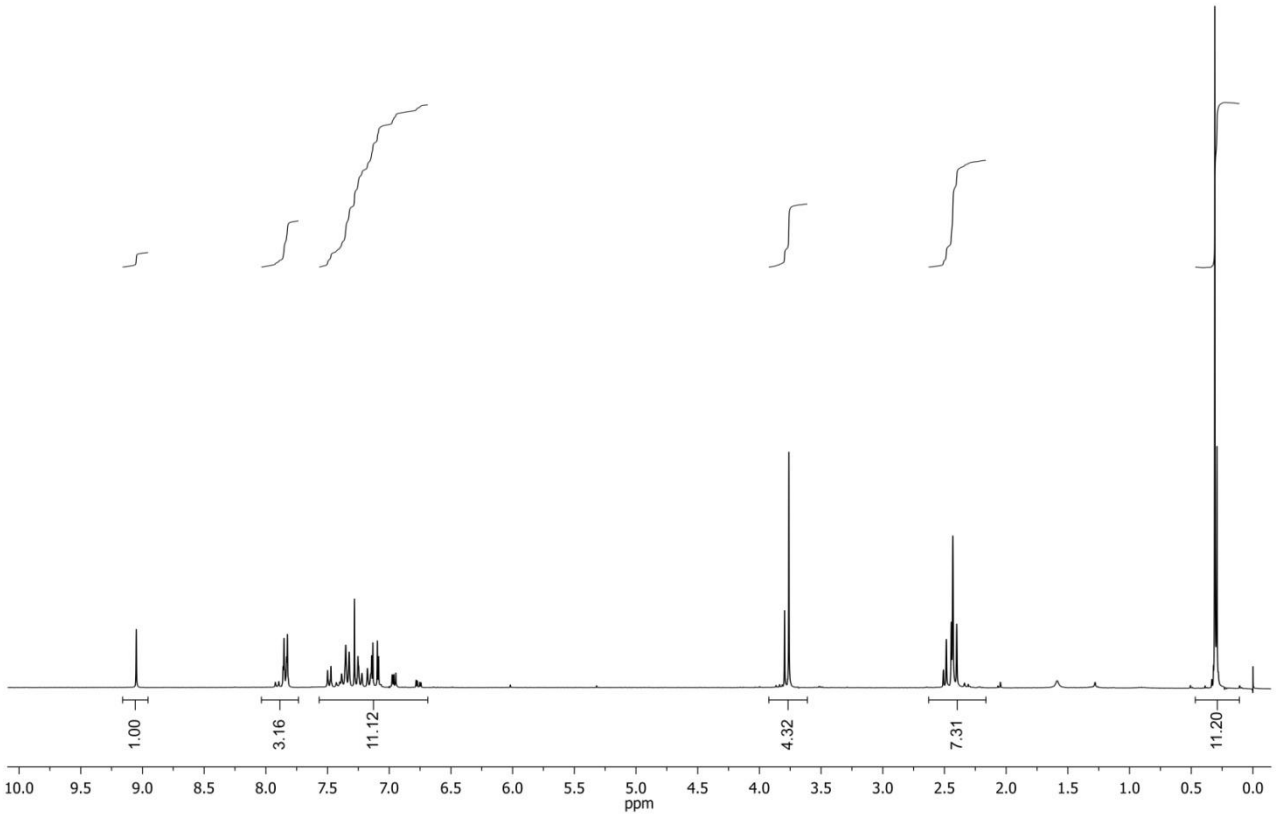


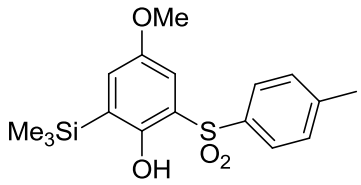


+ **2g**

3g

3g, ^{1}H NMR of the mixture (δ, $CDCl_3$).





+ **2g**

3g

3g, ^{13}C NMR of the mixture (δ, $CDCl_3$).