Exploring Substituent Effects in Reversible Photoswitchable Low Molecular Weight Arylazoisoxazole Adhesives

Luca Burg, Luuk Kortekaas, Anna Gibalova, Constantin Daniliuc, Janis Heßling, Monika Schönhoff and Bart Jan Ravoo

Electronic Supplementary Information

Additional Figures

Photoswitching

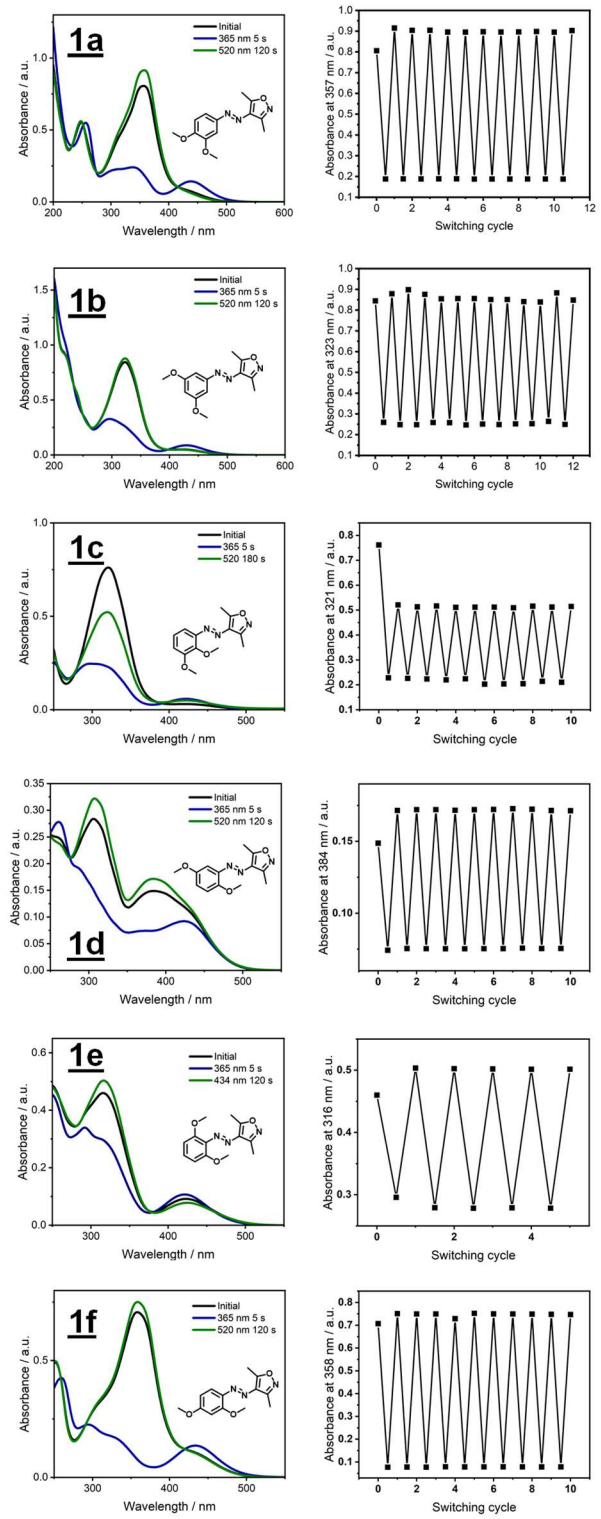


Figure S1. Absorbance spectra of dimethoxy-AIZ **1a-f**, c = 50 µmol/L in acetonitrile, initially (black line), after irradiation with UV-light (λ = 365 nm, blue line) and after irradiation with green light (λ = 520 nm, green line) and the cycled absorbance at the respective absorption maximum (**1a-d** and **1f**).

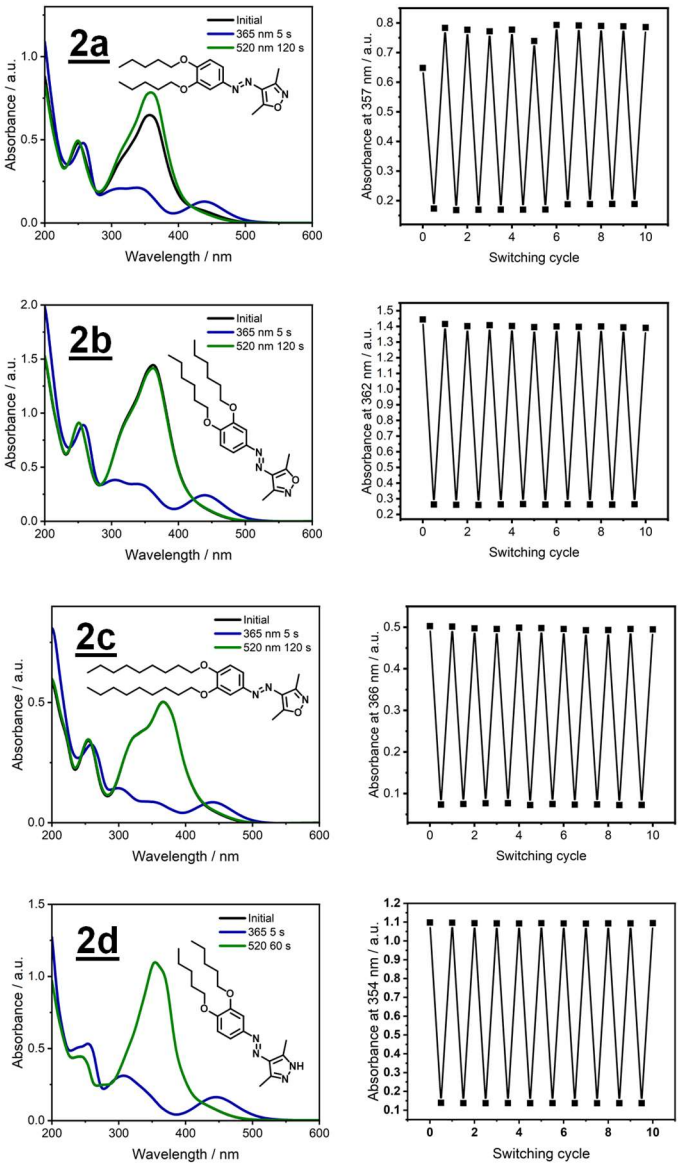


Figure S2. Absorbance spectra of dialkoxy-AIZ **2a-d**, c = 50 µmol/L in acetonitrile, initially (black line), after irradiation with UV-light (λ = 365 nm, blue line) and after irradiation with green light (λ = 520 nm, green line) and their cycled absorbance at the respective absorption maximum.

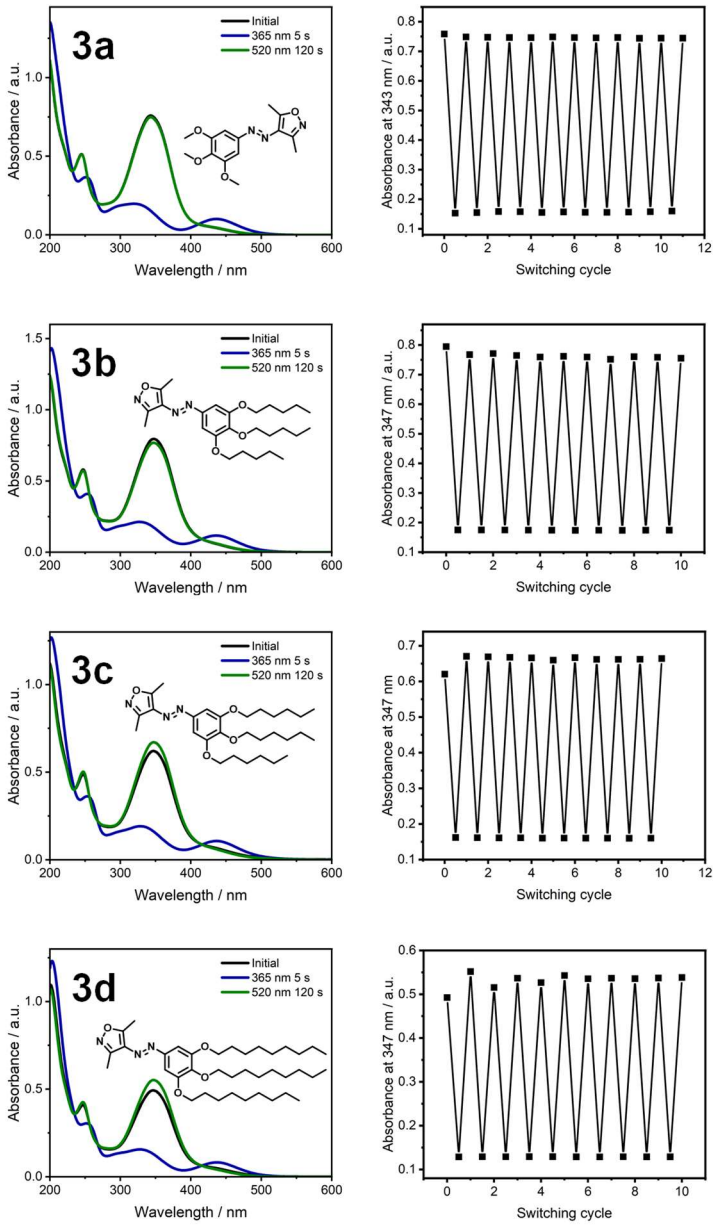


Figure S3. Absorbance spectra of trialkoxy-AIZ **2a-d**, c = 50 µmol/L in acetonitrile, initially (black line), after irradiation with UV-light (λ = 365 nm, blue line) and after irradiation with green light (λ = 520 nm, green line) and their cycled absorbance at the respective absorption maximum.

Photostationary States

Table S1. Photostationary states and half-life times of **1a**, **2a**, **2d**, **3a** and **3b**.

Compound	PSS 365	PSS 520	$T_{1/2}$ 25C	Initial
1a	92:8	95:5	206 d	>99%
2a	90:10	94:6	89 d	95:5
2d	95:5	95:5	24 min	83:17
3a	93:7	92:8	105 d	>99%
3b	94:6	92:8	40 d	85:15

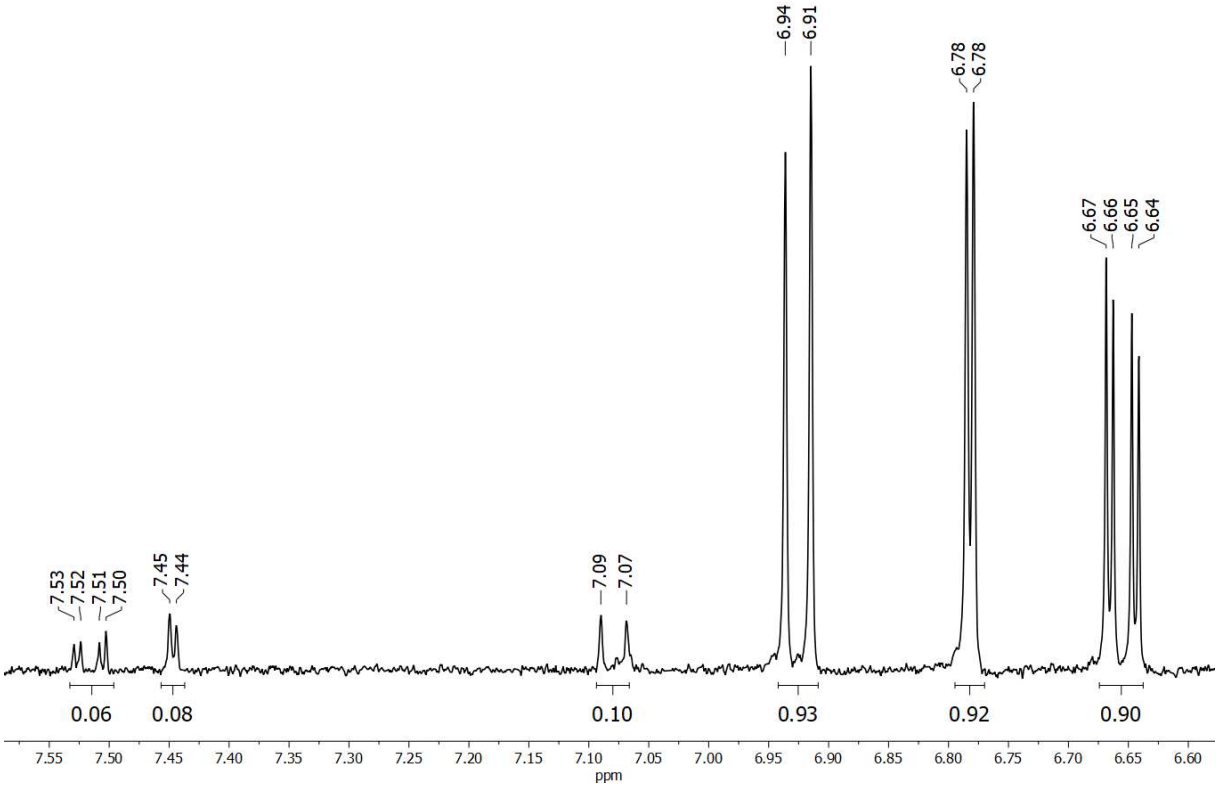


Figure S4. Aromatic region of a ^{1}H-NMR spectra of AIZ **1a** after irradiation with UV-light (λ = 365 nm) to.

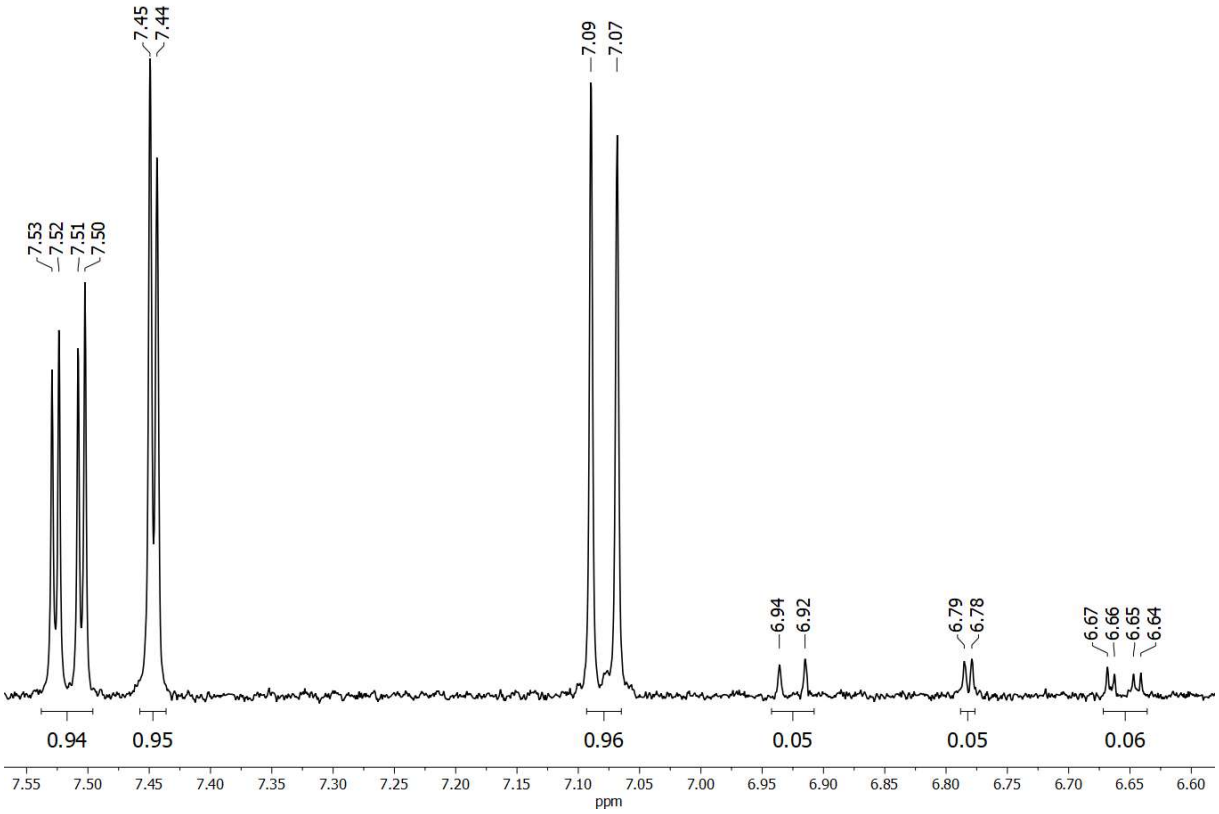


Figure S5. Aromatic region of a ^{1}H-NMR spectra of AIZ **1a** after irradiation with green light (λ = 520 nm).

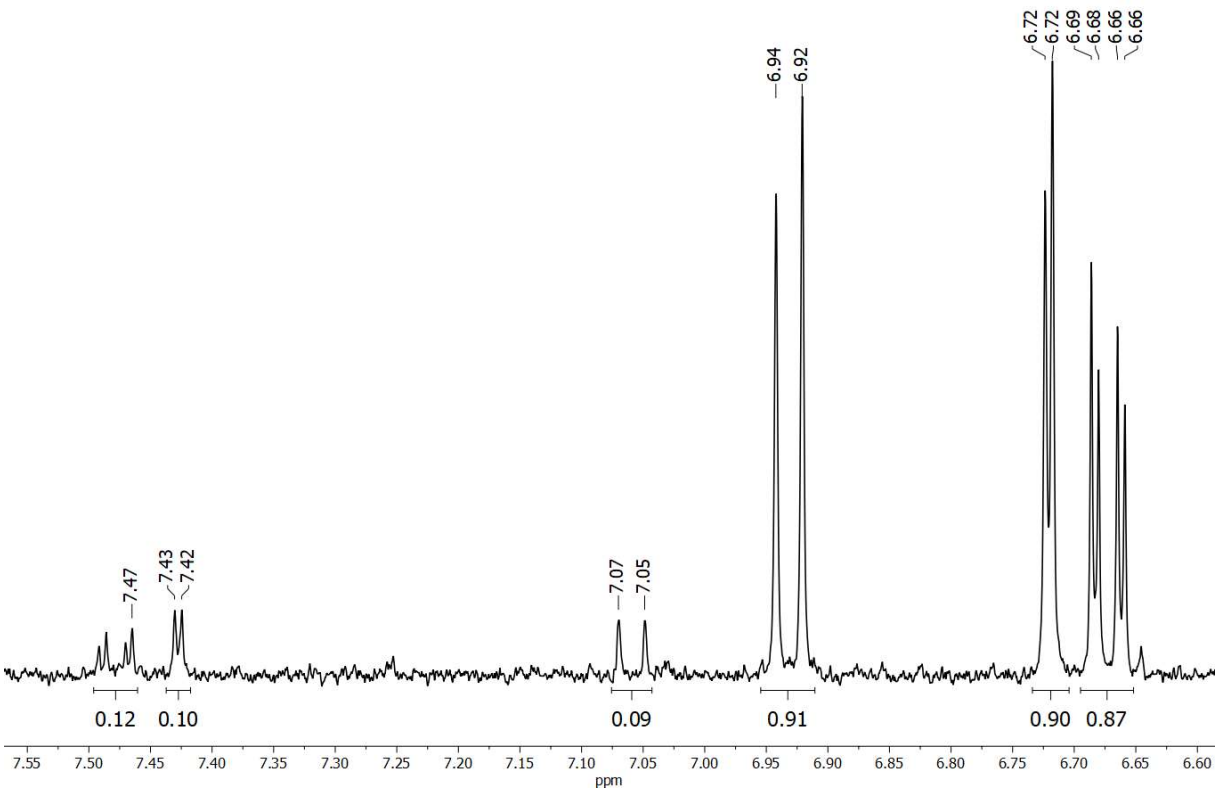


Figure S6. Aromatic region of a ^{1}H-NMR spectra of AIZ **2a** after irradiation with UV-light (λ = 365 nm).

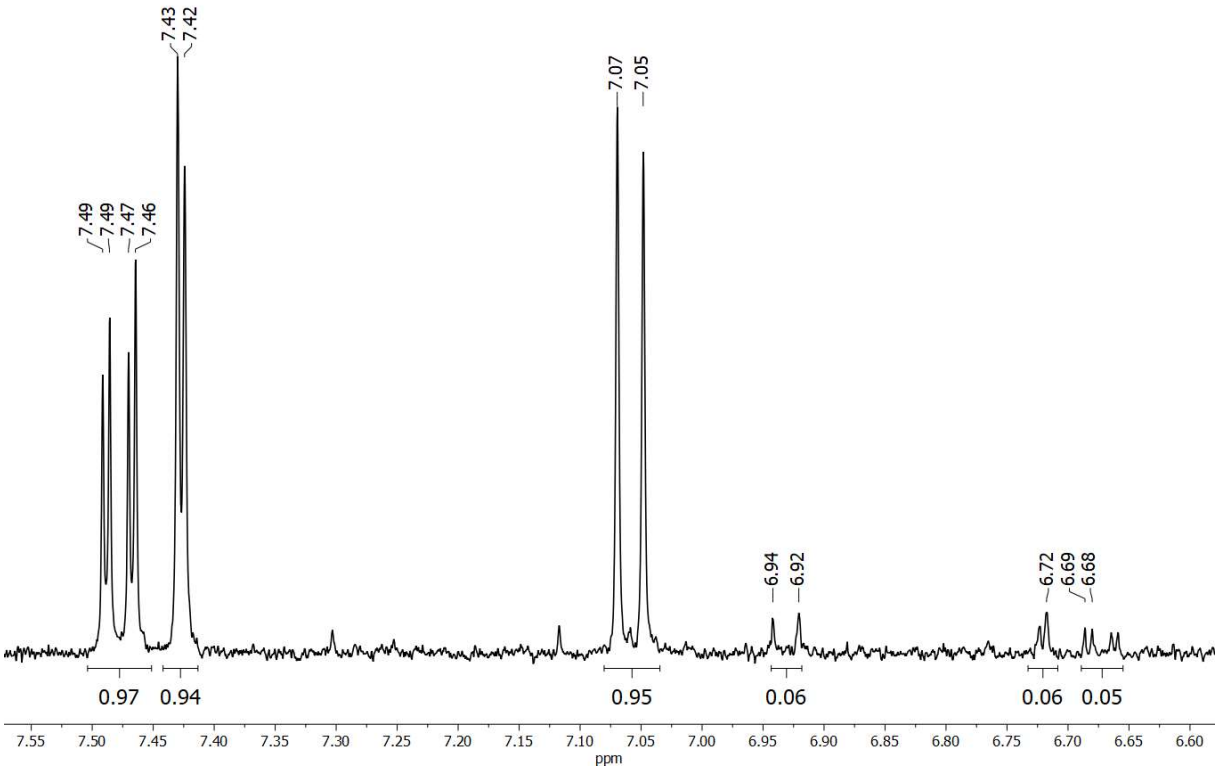


Figure S7. Aromatic region of a ^{1}H-NMR spectra of AIZ **2a** after irradiation with green light (λ = 520 nm).

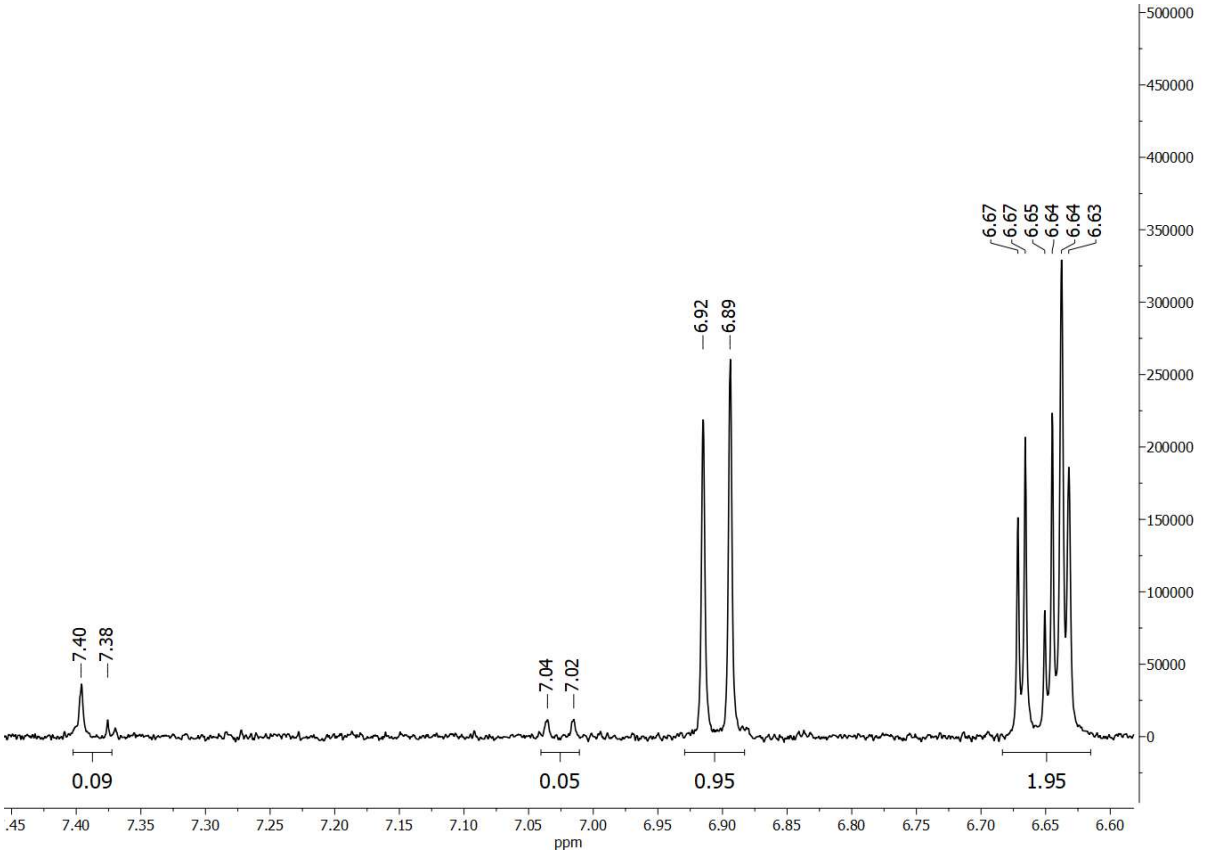


Figure S8. Aromatic region of a ^{1}H-NMR spectra of AAP **2d** after irradiation with UV-light (λ = 365 nm).

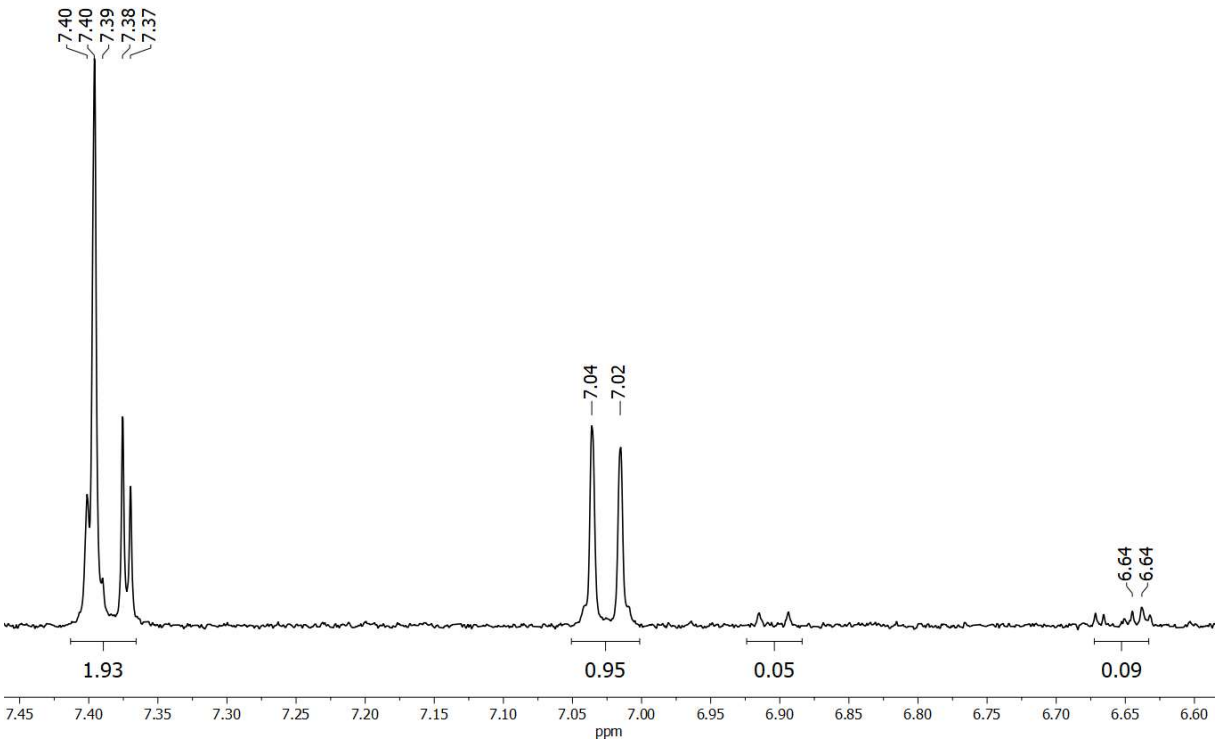


Figure S9. Aromatic region of a ^{1}H-NMR spectra of AAP **2d** after irradiation with green light (λ = 520 nm).

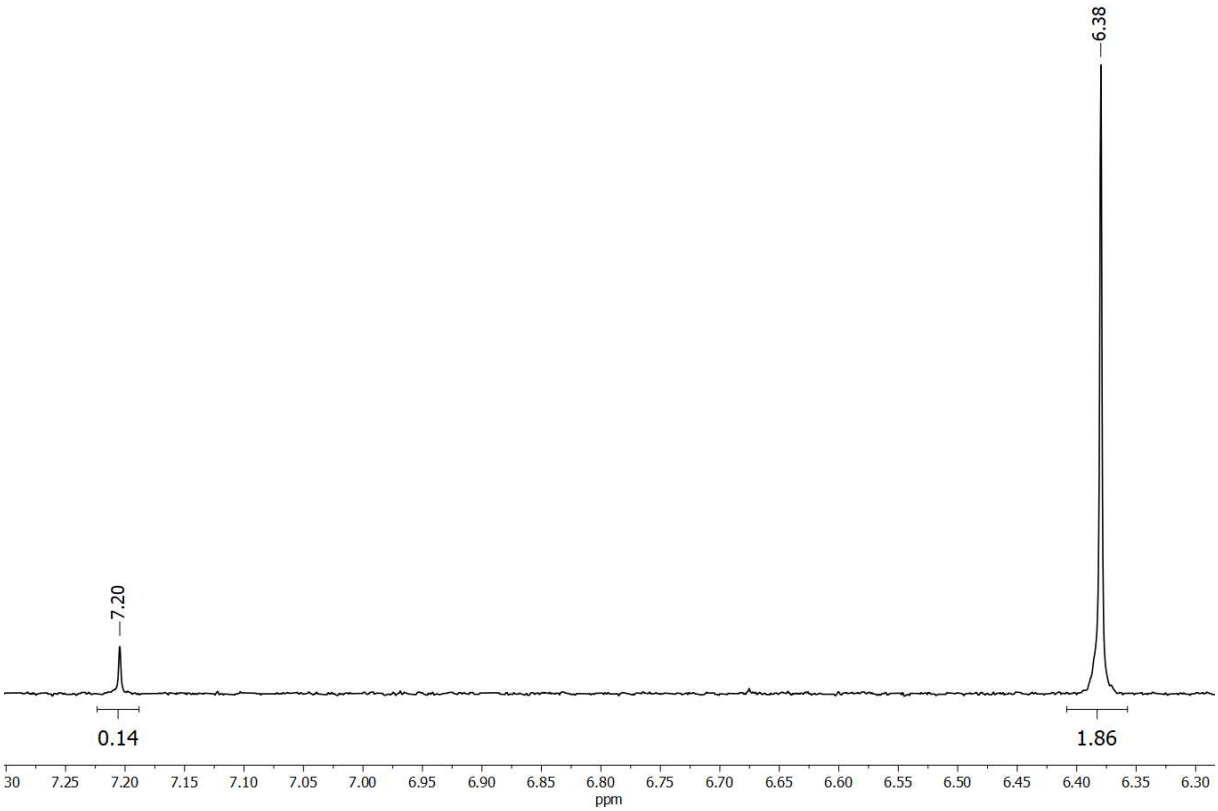


Figure S10. Aromatic region of a ^{1}H-NMR spectra of AIZ **3a** after irradiation with UV-light (λ = 365 nm).

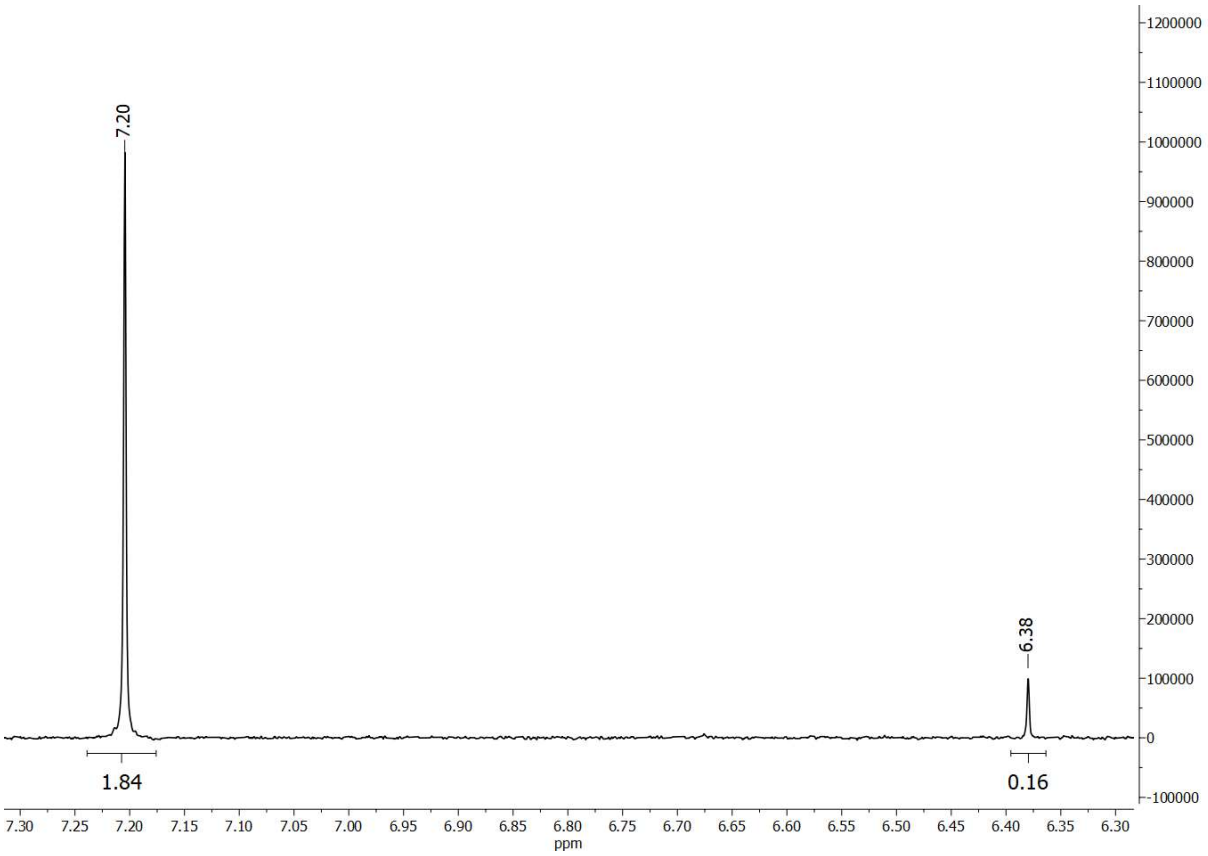


Figure S11. Aromatic region of a ^{1}H-NMR spectra of AIZ **3a** after irradiation with green light (λ = 520 nm).

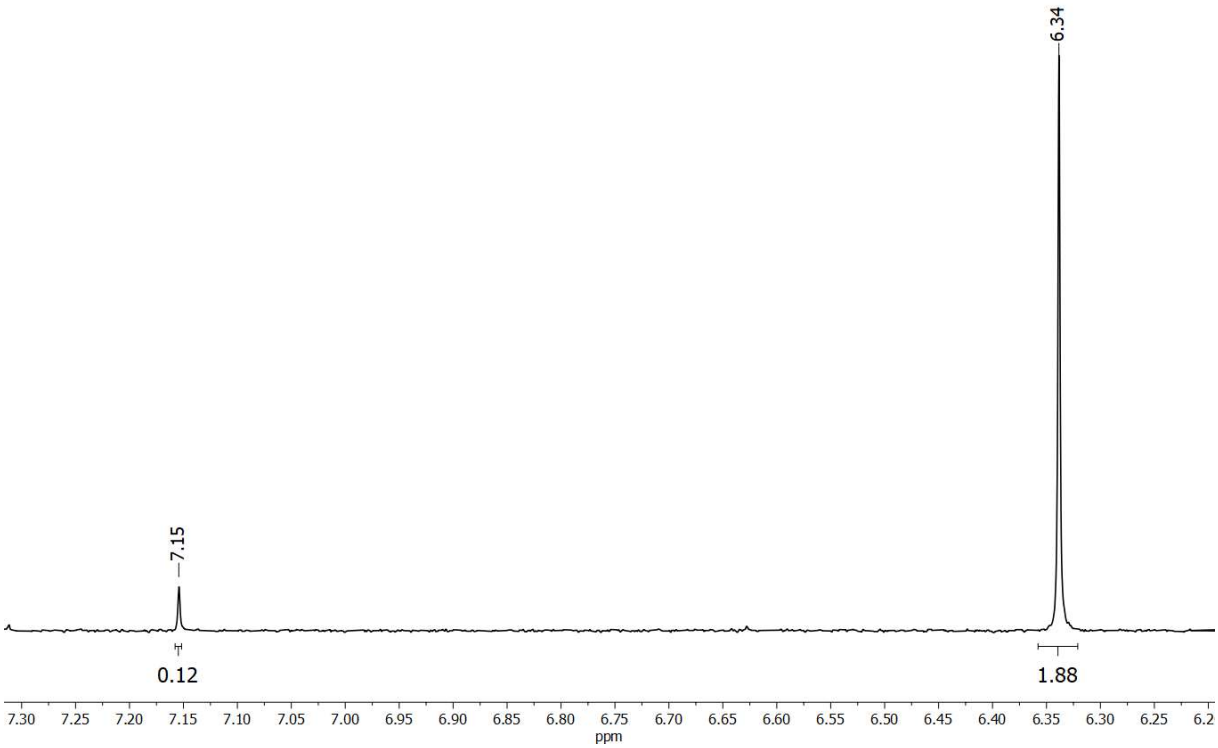


Figure S12. Aromatic region of a ^{1}H-NMR spectra of AIZ **3b** after irradiation with UV-light (λ = 365 nm).

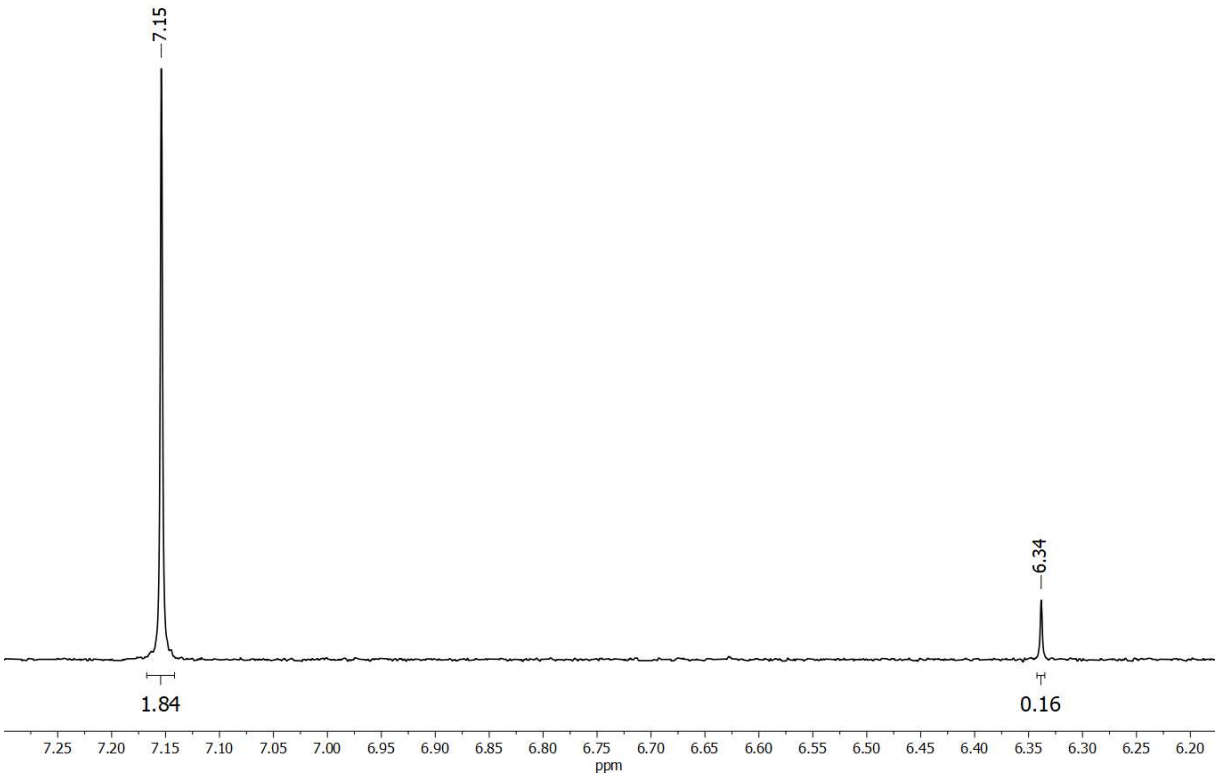


Figure S13. Aromatic region of a ^{1}H-NMR spectra of AIZ **3b** after irradiation with green light (λ = 520 nm).

Microscopy Images

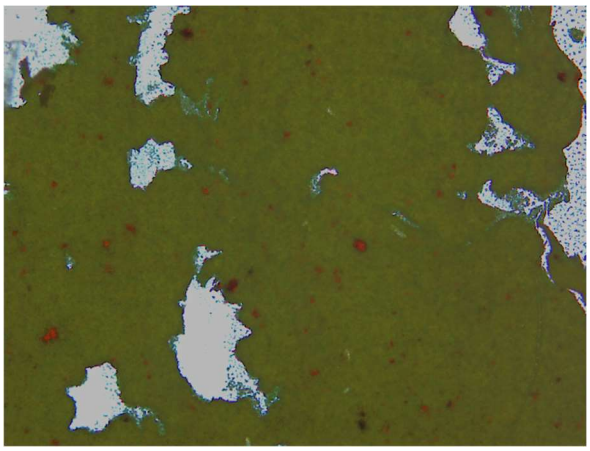


Figure S14. Photocured AIZ **1a** on a glass slide after an adhesive test under a light microscope with 10x magnification.

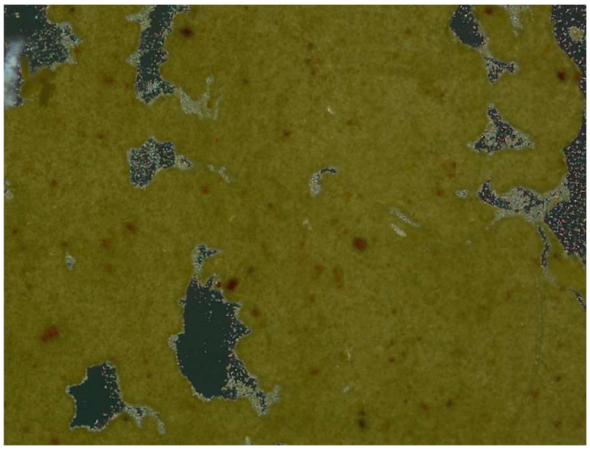


Figure S15. Photocured AIZ **1a** on a glass slide after an adhesive test under polarized light microscopy with 10x magnification, showing crystalline behaviour.

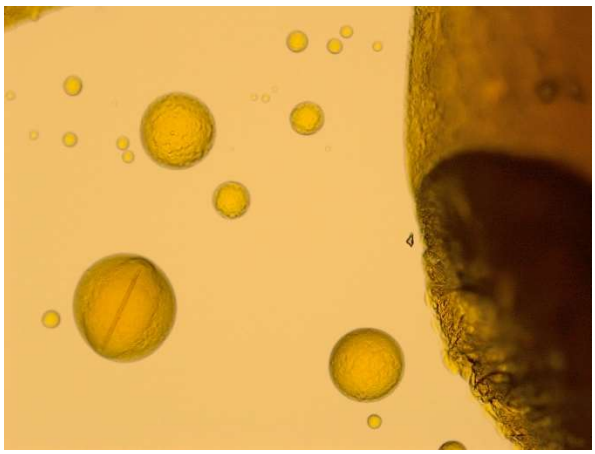


Figure S16. Partial crystalline behavior of the dipentoxy-AAP **2e** under a light microscope with 10x magnification after irradiation with UV-light (λ = 365 nm, 2 min).

Experimental Procedures

Adhesion Experiments

To determine the adhesive strength, glass slides with a size of 1.4 by 2.4 cm with an overlapping area in a size of 1 by 1.4 cm were used. The examined amount of the adhesive was ~2.1 mg per test run. After placing the adhesive on the glass substrate, the adhesive was irritated by UV-light (λ = 365 nm) yielding the solid-to-liquid phase transition. After complete photo liquification (after 30-120 seconds) two glass substrates were pressed together, fixed with an ordinary clothespin, and irritated by green light (λ = 520 nm), yielding the liquid-to-solid phase transition (after 180-360 seconds). The determination of the weight bearing capacity was conducted by placing the conjoined glass slides in each a metal slide holder, which made it possible to adhere weights. Weights were added in 100 g steps until the failure of the glue. This procedure was repeated 10 times, to gain an average maximum weight bearing capacity. Further, we analyzed the reversibility of the adhesive system and conducted 10 cycles of gluing with the same sample, according to the mentioned above procedure.

Synthesis

AIZ **1a-f 3a-d** were synthesized according to general procedures I and II, starting from the corresponding amines, as seen in **Figure S17**. Starting reagents for the AIZ **1a-f** and **3a** were commercially available, while starting reagents for the AIZ **3b-d** had to be synthesized according to the general procedures IV-IX (**Figure S18**).

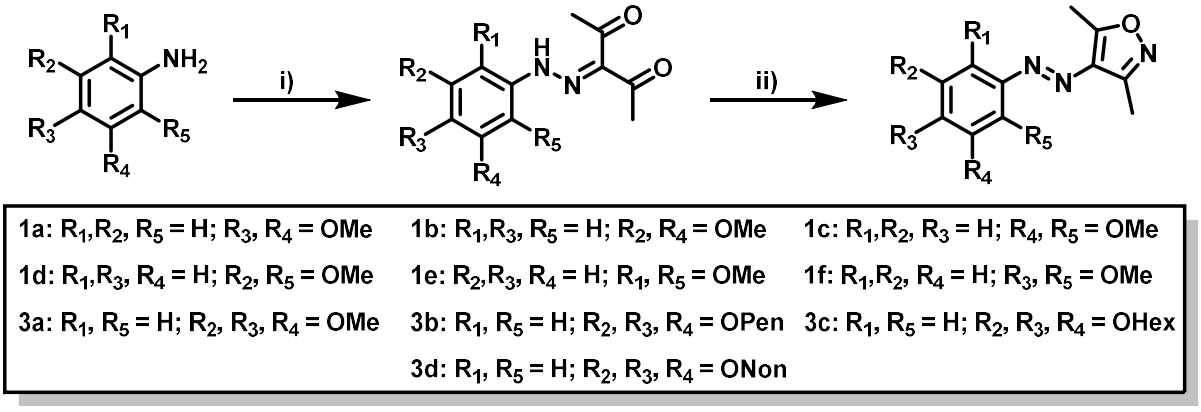


Figure S17. Synthesis of AIZ **1a-f** and **3a-d**. i) AcOH, HCl, $NaNO_2$, 0 °C, 30 min; H_2O, EtOH, pentane-2,4-dione, NaAcO, r.t., 45 min. ii) hydroxyl amine hydrochloride, Na_2CO_3, EtOH, 80 °C, overnight.

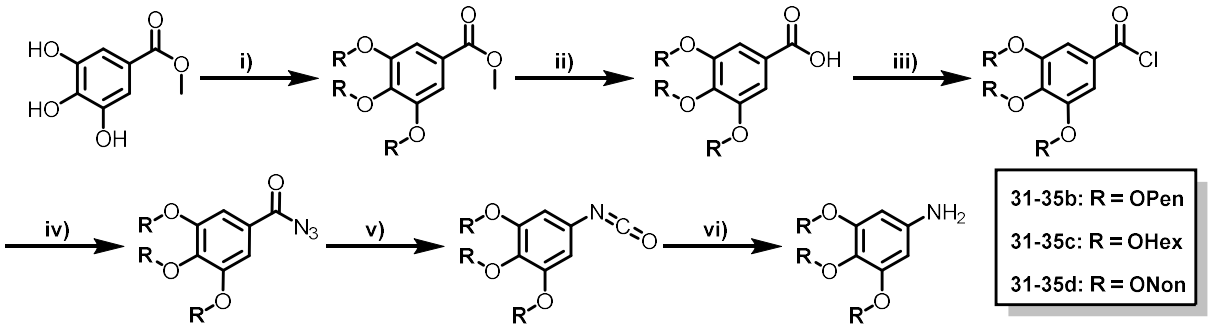


Figure S18. Synthesis of the precursors for 3b-d. i) Br-R, K_2CO_3, DMF, 80°C, overnight; ii) KOH, EtOH, H_2O, 100°C, 5h; iii) $SOCl_2$, DCM, r.t., overnight; iv) NaN_3, THF, H_2O, 0°C, 5h; v) toluene, 110°C, overnight; vi) KOH, 1,4-dioxane, H_2O, 90°C, overnight.

AIZ **2a-c** were synthesized starting from the deprotection of AIZ **1a** followed by the general procedure III (**Figure S19**).

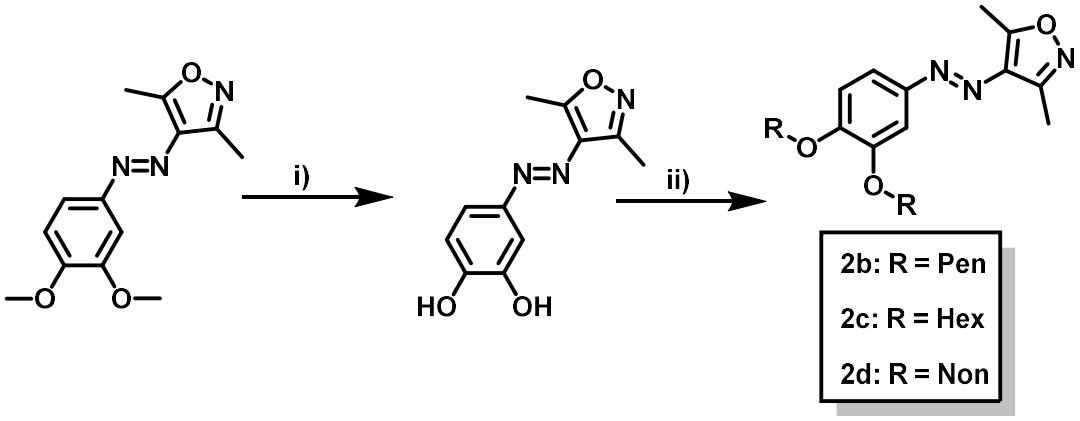


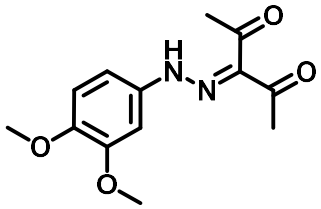
Figure S19. Synthesis of **2a-c**. i) BBr_3, toluene, DCM, -70°C to r.t., 5h; ii) Br-R, K_2CO_3, DMF, r.t., overnight.

Synthesis of AIZ 1a-f and 3a-d

General Procedure I: Dione synthesis

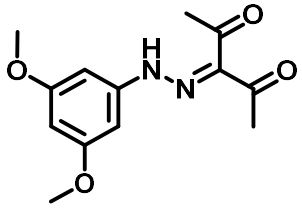
The substituted aniline (1.0 eq.) was stirred in AcOH (1.5 mL/mmol) and concentrated HCL (0.23 mL/mmol) and cooled to 0 °C. $NaNO_2$ (1.2 eq.) dissolved in a small amount of H_2O was added to the solution dropwise. The resulting mixture was stirred for 45 min at 0 °C. The resulting mixture was added to a solution of NaOAc (3.0 eq.) and pentane-2,4-dione (1.3 eq.) in H_2O (0.6 mL/mmol) and EtOH (1.0 mL/mmol). After stirring for 60 min at room temperature, the precipitate was filtered and washed several times with water, yielding the desired compound in a yellow-orange solid.

3-(2-(3,4-dimethoxyphenyl)hydrazineylidene)pentane-2,4-dione (11a)



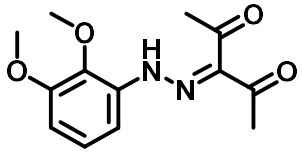
Yield: 6.61 g (100%). **1H-NMR** (400 MHz, CDCl3): δ = 14.95 (s, 1H), 7.06 (d, *J* = 2.3 Hz, 1H), 6.96 – 6.86 (m, 2H), 3.92 (d, *J* = 11.8 Hz, 6H), 2.60 (s, 3H), 2.48 (s, 3H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 197.81, 196.99, 150.33, 147.81, 135.56, 132.90, 111.87, 108.84, 100.17, 56.39, 56.12, 31.71, 26.72 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{13}H_{16}N_2O_4Na]^+$: 287.10023; found 287.10017 $[M+Na]^+$.

3-(2-(3,5-dimethoxyphenyl)hydrazineylidene)pentane-2,4-dione (11b)



Yield: 0.90 g (69%). **1H-NMR** (400 MHz, CDCl3): δ = 14.59 (s, 1H), 6.57 (d, *J* = 2.2 Hz, 2H), 6.30 (s, 1H), 3.82 (s, 6H), 2.60 (s, 3H), 2.48 (s, 3H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 198.16, 197.22, 161.90, 143.51, 133.29, 98.00, 94.97, 55.65, 31.86, 26.76 ppm.

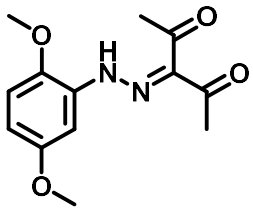
3-(2-(2,3-dimethoxyphenyl)hydrazineylidene)pentane-2,4-dione (11c)



Yield: 2.53 g (96%). **1H-NMR** (400 MHz, CDCl3): δ = 14.77 (s, 1H), 7.40 – 7.32 (m, 1H), 7.10 (td, J = 8.3, 0.7 Hz, 1H), 6.75 (dd, J = 8.3, 1.4 Hz, 1H), 3.97 (s, 3H),

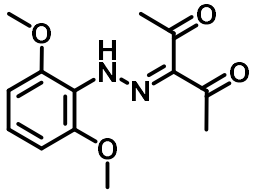
3.90 (s, 3H), 2.61 (s, 3H), 2.49 (s, 3H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 197.59, 197.42, 153.13, 138.36, 135.69, 133.98, 124.82, 109.28, 107.80, 61.17, 56.15, 31.80, 26.80 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{13}H_{16}N_2O_4Na]^+$: 287.10023; found 287.10002 [M+Na]+.

3-(2-(2,5-dimethoxyphenyl)hydrazineylidene)pentane-2,4-dione (11d)



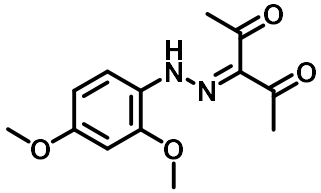
Yield: 2.43 g (92%). **1H-NMR** (400 MHz, CDCl3): δ = 14.72 (s, 1H), 7.31 (d, *J* = 3.0 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.69 (dd, *J* = 8.9, 3.0 Hz, 1H), 3.92 (s, 3H), 3.82 (s, 3H), 2.61 (s, 3H), 2.50 (s, 3H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 197.46, 197.39, 154.71, 143.19, 133.92, 131.65, 112.36, 110.65, 101.64, 56.57, 55.91, 31.77, 26.80 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{13}H_{16}N_2O_4Na]^+$: 287.10023; found 287.10033 [M+Na]+.

3-(2-(2,6-dimethoxyphenyl)hydrazineylidene)pentane-2,4-dione (11e)



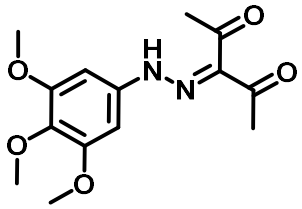
Yield: 2.15 g (81%). **1H-NMR** (400 MHz, CDCl3): δ = 14.67 (s, 1H), 7.14 (t, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 3.91 (s, 6H), 2.59 (s, 3H), 2.42 (s, 3H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 197.89, 197.03, 152.40, 133.77, 126.79, 119.79, 105.07, 56.50, 31.63, 26.61 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{13}H_{16}N_2O_4Na]^+$: 287.10023; found 287.10009 [M+Na]+.

3-(2-(2,4-dimethoxyphenyl)hydrazineylidene)pentane-2,4-dione (11f)



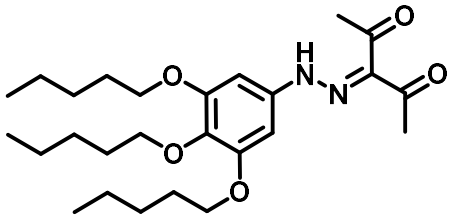
Yield: 1.65 g (63%). **1H-NMR** (400 MHz, CDCl3): δ = 14.96 (s, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 6.57 (ddd, *J* = 8.8, 2.5, 0.6 Hz, 1H), 6.53 (d, *J* = 2.5 Hz, 1H), 3.94 (s, 3H), 3.83 (s, 3H), 2.60 (s, 3H), 2.48 (s, 3H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 197.31, 197.07, 158.96, 150.00, 133.34, 124.95, 116.31, 105.69, 98.97, 56.12, 55.82, 31.63, 26.80 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{13}H_{16}N_2O_4Na]^+$: 287.10023; found 287.10019 [M+Na]+.

3-(2-(3,4,5-trimethoxyphenyl)hydrazineylidene)pentane-2,4-dione (37a)



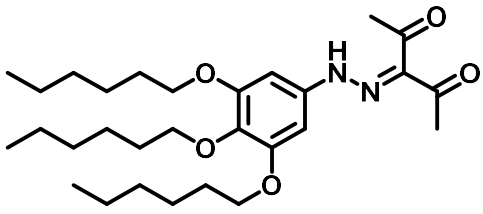
Yield: 0.86 g (59%). **1H-NMR** (400 MHz, CDCl3): δ = 14.88 (s, 1H), 6.75 (s, 2H), 3.99 (s, 6H), 3.94 (s, 3H), 2.70 (s, 3H), 2.58 (s, 3H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 198.08, 196.98, 154.36, 137.74, 136.43, 133.14, 93.84, 93.77, 61.25, 56.32, 31.83, 26.71 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{14}H_{18}N_2O_5Na]^+$: 317.11079; found 317.11057 [M+Na]+

3-(2-(3,4,5-tris(pentyloxy)phenyl)hydrazineylidene)pentane-2,4-dione (37b)



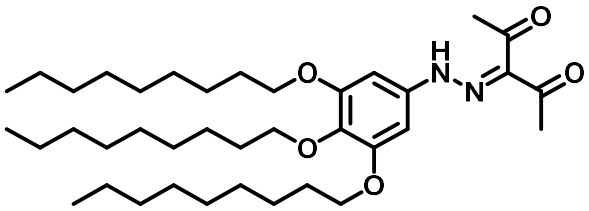
Yield: 1.64 g (83%). **1H-NMR** (400 MHz, CDCl3): δ = 14.79 (s, 1H), 6.62 (s, 2H), 4.01 – 3.93 (m, 6H), 2.60 (s, 3H), 2.47 (s, 3H), 1.86 – 1.72 (m, 6H), 1.51 – 1.35 (m, 12H), 0.95 – 0.91 (td, J = 7.2, 4.0 Hz, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 197.90, 197.08, 154.20, 137.25, 95.24, 77.48, 77.16, 76.84, 73.79, 69.35, 31.76, 30.09, 29.10, 28.39, 26.70, 22.70, 22.59, 14.22, 14.18 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{26}H_{42}N_2O_5Na]$+: 485.29859; found 485.29861 [M+Na]+.

3-(2-(3,4,5-tris(hexyloxy)phenyl)hydrazineylidene)pentane-2,4-dione (37c)



Yield: 1.68 g (87%). **1H-NMR** (400 MHz, CDCl3): δ = 14.78 (s, 1H), 6.62 (s, 2H), 3.97 (d, *J* = 21.6 Hz, 6H), 2.60 (s, 3H), 2.47 (s, 3H), 1.87 – 1.67 (m, 6H), 1.48 (tdd, *J* = 10.0, 4.3, 2.3 Hz, 6H), 1.34 (s, 12H), 0.91 (s, 9H) ppm. **ESI-HRMS** (m/z): Calculated for $[C_{29}H_{48}N_2O_5Na]$+: 527.34554; found 527.34534 [M+Na]+.

3-(2-(3,4,5-tris(nonyloxy)phenyl)hydrazineylidene)pentane-2,4-dione (37d)

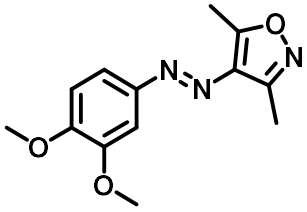


Yield: 1.63 g (90%). **1H-NMR** (400 MHz, CDCl3): δ = 7.46 (s, 2H) 4.31 - 4.13 (m, 6H), 2.95 (d, *J* = 11.4 Hz, 3H), 2.74 (d, *J* = 15.1 Hz, 3H), 2.06 – 1.94 (m, 6H), 1.69 (q, *J* = 6.5 Hz, 6H), 1.52 (m, 30H), 1.08 (s, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 168.69, 154.01, 153.58, 148.73, 140.91, 132.42, 101.11, 73.80, 69.31, 32.10, 32.06, 30.51, 29.84, 29.75, 29.57, 29.53, 29.50, 29.45, 26.28, 26.25, 22.84, 14.25, 12.26, 11.90 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{38}H_{66}N_2O_5Na]$+: 653.48639; found 653.48599 [M+Na]+.

General Procedure II: AIZ ring closure

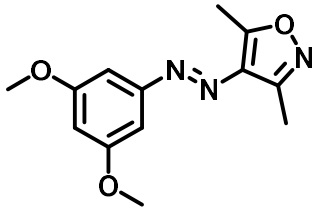
Product of Procedure I (1.0 eq.) was suspended in EtOH (10 mL/mmol) and Na_2CO_3 (1.5 eq.) and hydroxylamine hydrochloride (1.5 eq.) were added. The resulting mixture was stirred at 80 °C overnight. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, CH/EtOAc 10:1). The product was recrystallized and dried resulting in a yellow solid.

(E)-4-((3,4-dimethoxyphenyl)diazenyl)-3,5-dimethylisoxazole (1a)



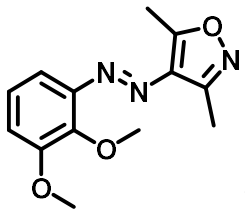
Yield: 3.15 g (32%). **1H-NMR** (400 MHz, CDCl3): δ = 7.50 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.38 (d, *J* = 2.2 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 3.97 (d, *J* = 1.8 Hz, 6H), 2.74 (s, 3H), 2.53 (s, 3H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 168.33, 154.08, 151.79, 149.73, 147.37, 132.37, 119.81, 110.57, 101.66, 56.29, 56.07, 12.28, 11.88 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{13}H_{15}N_3O_3Na]^+$: 284.10056; found 284.10048 $[M+Na]^+$.

(E)-4-((3,5-dimethoxyphenyl)diazenyl)-3,5-dimethylisoxazole (1b)



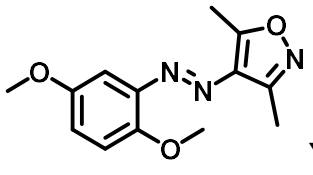
Yield: 0.32 g (37%). **1H-NMR** (400 MHz, CDCl3): δ = 6.99 (d, *J* = 2.3 Hz, 2H), 6.57 (t, *J* = 2.3 Hz, 1H), 3.86 (s, 6H), 2.75 (s, 3H), 2.52 (s, 3H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 169.70, 161.25, 154.84, 153.87, 132.47, 103.29, 100.51, 77.38, 55.73, 12.27, 11.88 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{13}H_{15}N_3O_3Na]^+$: 284.10056; found 284.10047 $[M+Na]^+$.

(E)-4-((2,3-dimethoxyphenyl)diazenyl)-3,5-dimethylisoxazole (1c)



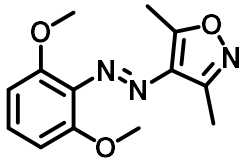
Yield: 0.17 g (64%). **1H-NMR** (400 MHz, CDCl3): δ = 7.21 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.09 (t, *J* = 8.1 Hz, 1H), 7.00 (dd, *J* = 8.1, 1.6 Hz, 1H), 4.01 (s, 3H), 3.93 (s, 3H), 2.76 (s, 3H), 2.56 (s, 3H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 169.68, 154.07, 153.82, 147.58, 147.09, 133.34, 124.38, 123.85, 114.35, 112.26, 111.98, 108.61, 62.66, 60.62, 56.39, 56.20, 12.17, 11.83, 10.66 ppm. **ESI-HRMS** (m/z): Calculated for [$C_{13}H_{15}N_3O_3Na$]+: 284.10056; found 284.10047 [M+Na]+.

(E)-4-((2,5-dimethoxyphenyl)diazenyl)-3,5-dimethylisoxazole (1d)



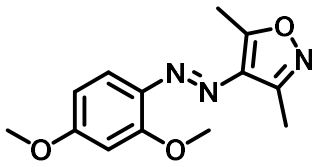
Yield: 0.59 g (50%). **1H-NMR** (400 MHz, CDCl3): δ = 7.20 – 7.15 (m, 1H), 7.04 – 6.96 (m, 2H), 3.96 (s, 3H), 3.82 (s, 3H), 2.75 (s, 3H), 2.54 (s, 3H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 168.81, 154.20, 151.87, 142.90, 133.38, 118.59, 114.98, 100.50, 57.54, 55.94, 12.01, 11.88 ppm. **ESI-HRMS** (m/z): Calculated for [$C_{13}H_{15}N_3O_3Na$]+: 284.10056; found 284.10048 [M+Na]+.

(E)-4-((2,6-dimethoxyphenyl)diazenyl)-3,5-dimethylisoxazole (1e)



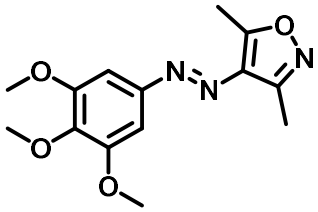
Yield: 0.48 g (44%). **1H-NMR** (400 MHz, CDCl3): δ = 7.22 (d, J = 8.4 Hz, 1H), 6.68 (d, J = 8.4 Hz, 2H), 3.83 (s, 6H), 2.71 (s, 3H), 2.50 (s, 3H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 153.99, 152.62, 129.55, 105.51, 56.63, 12.03, 11.85 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{13}H_{15}N_3O_3Na]+$: 284.10056; found 284.10040 [M+Na]+.

(E)-4-((2,4-dimethoxyphenyl)diazenyl)-3,5-dimethylisoxazole (1f)



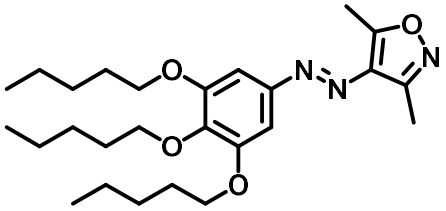
Yield: 0.32 g (40%). **1H-NMR** (400 MHz, CDCl3): δ = 7.65 (d, *J* = 8.9 Hz, 1H), 6.59 – 6.51 (m, 2H), 3.98 (s, 3H), 3.88 (s, 3H), 2.72 (s, 3H), 2.53 (s, 3H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 167.40, 163.58, 158.63, 154.42, 137.25, 117.70, 117.21, 105.75, 99.34, 56.52, 55.77, 11.95, 11.81 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{13}H_{15}N_3O_3Na]+$: 284.10056; found 284.10055 [M+Na]+.

(E)-3,5-dimethyl-4-((3,4,5-trimethoxyphenyl)diazenyl)isoxazole (3a)



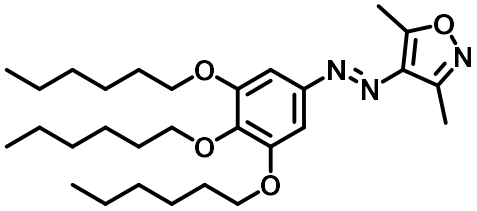
Yield: 0.14 g (16%). **1H-NMR** (400 MHz, CDCl3): δ = 7.11 (s, 2H), 3.95 (s, 6H), 3.92 (s, 3H), 2.75 (s, 3H), 2.54 (s, 3H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 169.11, 153.91, 153.70, 148.95, 140.58, 132.41, 130.17, 129.88, 123.80, 105.33, 99.81, 61.21, 60.99, 56.34, 56.21, 33.94, 32.06, 29.92, 29.83, 29.67, 29.47, 29.30, 29.20 (d, J = 3.4 Hz), 27.33 (d, J = 5.9 Hz), 24.84, 22.84, 14.27, 12.32, 11.93 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{14}H_{17}N_3O_4Na]^+$: 314.11113; found 314.11101 $[M+Na]^+$.

(E)-3,5-dimethyl-4-((3,4,5-tris(pentyloxy)phenyl)diazenyl)isoxazole (3b)



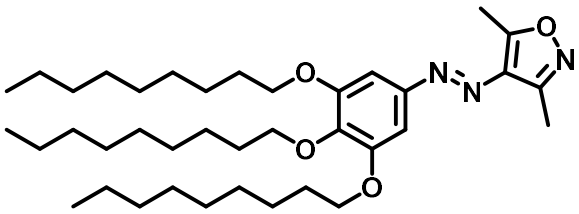
Yield: 0.53 g (33%). **1H-NMR** (400 MHz, CDCl3): δ = 7.06 (s, 2H), 4.05 (dt, *J* = 11.2, 6.5 Hz, 6H), 2.74 (s, 3H), 2.52 (s, 3H), 1.91 – 1.68 (m, 6H), 1.55 – 1.31 (m, 12H), 0.94 (td, *J* = 7.2, 3.6 Hz, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 168.70, 154.01, 153.57, 148.73, 101.08, 73.74, 69.28, 30.15, 29.15, 28.43, 28.37, 28.30, 22.70, 22.59, 14.23, 14.19, 12.26, 11.90 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{26}H_{41}N_3O_4Na]^+$: 482.29893; found 482.29891 $[M+Na]^+$.

(E)-3,5-dimethyl-4-((3,4,5-tris(hexyloxy)phenyl)diazenyl)isoxazole (3c)



Yield: 0.81 g (49%). **1H-NMR** (400 MHz, CDCl3): δ = 7.06 (s, 2H), 4.14 – 3.97 (m, 6H), 2.74 (s, 3H), 2.52 (s, 3H), 1.90 – 1.71 (m, 6H), 1.50 (tt, *J* = 11.3, 5.6 Hz, 6H), 1.35 (tq, *J* = 7.2, 3.8 Hz, 12H), 0.95 – 0.86 (m, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 168.69, 154.00, 153.57, 148.73, 140.90, 132.41, 101.09, 73.78, 69.30, 53.56, 31.91, 31.72, 30.45, 29.44, 25.93, 25.89, 22.83, 22.77, 14.23, 14.17, 12.25, 11.90 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{29}H_{47}N_3O_4Na]^+$: 524.34588; found 524.34534 $[M+Na]^+$.

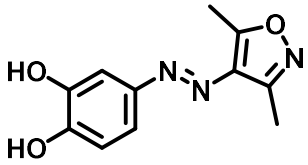
(E)-3,5-dimethyl-4-((3,4,5-tris(nonyloxy)phenyl)diazenyl)isoxazole (3d)



Yield: 0.09 g (18%). **1H-NMR** (400 MHz, CDCl3): δ = 7.46 (s, 2H), 4.31 – 4.13 (m, 6H), 2.95 (d, *J* = 11.4 Hz, 3H), 2.74 (d, *J* = 15.1 Hz, 3H), 2.06 – 1.94 (m, 6H), 1.70 – 1.66 (m, 6H), 1.56 – 1.48 (m, 30H), 1.08 (s, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 168.69, 154.01, 153.58, 148.73, 140.91, 132.42, 101.11, 74.35, 73.80, 69.31, 32.10, 32.06, 30.51, 29.84, 29.75, 29.68, 29.57, 29.53, 29.50, 29.45, 26.28, 26.25, 22.85, 22.84, 14.25, 12.34, 12.26, 11.90 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{38}H_{65}N_3O_4Na]^+$: 650.48673; found 650.48248 $[M+Na]^+$.

Synthesis of 2a-c

(E)-4-((3,5-dimethylisoxazol-4-yl)diazenyl)benzene-1,2-diol (21)



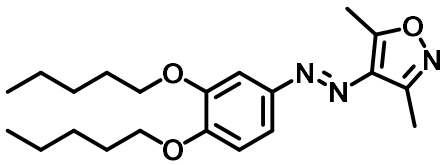
The Dimethoxy-AIZ **1a** was dissolved in toluene (10 mL/mmol) and cooled to -70 °C. A solution of BBr_3 (1M in DCM) was added dropwise, while temperature was kept below -70 °C. The resulting mixture was stirred for 5 h while warming up to room temperature. Methanol (5 mL/mmol) was added to the solution and stirred for further 30 min. The solvent was removed, and the crude product was purified by column chromatography (silica, CH/EtOAc 4:1). The product was received as a dark red solid and used immediately without further purification.

Yield: 0.17 g (74%).

General Procedure III: Synthesis of AIZ 2a-c

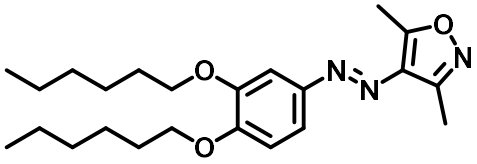
Compound **21** (1.0 eq.) was dissolved in DMF (10 mL/mmol) and K_2CO_3 (6.0 eq.) and the corresponding bromo alkane (6.0 eq.) were added. The solution was stirred overnight at room temperature. The crude product was extracted with DCM (2x 30 mL) and washed with H_2O (2x 30 mL) and brine (1x 30 mL). The organic layer was dried with $MgSO_4$, and the solvent was removed. The crude product was purified by column chromatography (silica, CH:EtOAc 10:1). The product was recrystallized and received as yellow solid.

(E)-4-((3,4-bis(pentyloxy)phenyl)diazenyl)-3,5-dimethylisoxazole (2a)



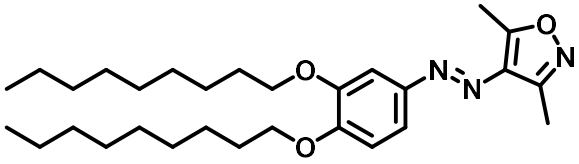
Yield: 0.04 g (15%). **1H-NMR** (400 MHz, CDCl3): δ = 7.30 (d, *J* = 2.9 Hz, 1H), 7.17 (s, 1H), 6.99 - 6.94 (m, 1H), 4.05 (dq, *J* = 12.5, 5.9 Hz, 4H), 2.76 – 2.73 (m, 3H), 2.58 – 2.53 (m, 3H), 1.91 – 1.81 (m, 4H), 1.26 (s, 8H), 0.97 – 0.84 (m, 6H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 143.37, 116.56, 113.70, 101.03, 100.66, 69.61, 69.59, 69.53, 69.46, 29.86, 29.00, 28.88, 28.86, 28.82, 28.40, 28.35, 28.28, 22.62, 22.59, 22.56, 14.19, 14.16, 12.55, 12.35, 12.05, 11.98, 11.86 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{21}H_{31}N_3O_3H]$+: 374.24382; found 374.24388 [M+H]+.

(E)-4-((3,4-bis(hexyloxy)phenyl)diazenyl)-3,5-dimethylisoxazole (2b)



Yield: 0.12 g (36%). **1H-NMR** (400 MHz, CDCl3): δ = 7.46 – 7.36 (m, 1H), 7.30 – 7.29 (m, 1H), 6,99 – 6.94 (m, 1H), 4.09 – 4.01 (m, 4H), 2.76 – 2.73 (m, 3H), 2.58 – 2.53 (m, 3H), 1.90 – 1.80 (m, 4H), 1.51 – 1.47 (m, 4H), 1.38 – 1.33 (m, 8H), 0.94 – 0.90 (m, 6H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 168.84, 168.72, 168.07, 154.16, 154.14, 152.58, 152.54, 152.05, 149.70, 149.07, 148.50, 147.33, 143.36, 132.37, 119.45, 119.07, 116.56, 113.71, 112.50, 104.18, 101.05, 100.68, 69.61, 69.59, 69.55, 69.48, 69.40, 69.34, 31.74, 31.73, 31.70, 31.65, 29.28, 29.17, 29.15, 29.09, 25.87, 25.82, 25.76, 22.75, 22.73, 14.16, 14.14, 12.55, 12.35, 12.22, 12.05, 11.98, 11.86 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{23}H_{35}N_3O_3Na]$+: 424.25706; found 424.25712 [M+Na]+.

(E)-4-((3,4-bis(nonyloxy)phenyl)diazenyl)-3,5-dimethylisoxazole (2c)



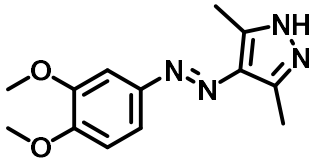
Yield: 0.10 g (12%). **1H-NMR** (400 MHz, CDCl3): δ = 7.27 (s, 1H), 7.23 (s, 1H), 7.13 (s, 1H), 4.02 (dq, *J* = 12.1, 5.8 Hz, 4H), 2.73 (s, 3H), 2.55 (s, 3H), 1.86 – 1.76 (m, 4H), 1.47 – 1.41 (m, 4H), 1.36 – 1.24 (m, 20H), 0.85 (dt, *J* = 7.1, 3.4 Hz, 6H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 168.83, 154.16, 152.58, 152.05, 149.70, 149.07, 148.50, 147.33, 143.36, 142.25, 133.03, 129.23, 119.43, 119.07, 116.58, 113.72, 112.52, 104.21, 101.07, 100.70, 69.61, 69.59, 69.56, 69.49, 69.40, 69.36, 32.04, 29.74, 29.72, 29.70, 29.59, 29.55, 29.50, 29.43, 29.41, 29.34, 29.32, 29.23, 29.21, 29.13, 26.21, 26.16, 26.09, 22.83, 14.25, 12.55, 12.34, 12.22, 12.04, 11.98, 11.86 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{29}H_{47}N_3O_3Na]$+: 508.35096; found 508.35096 [M+Na]+.

Synthesis of 2d-e

General Procedure IV: Synthesis of AAP 2d-e

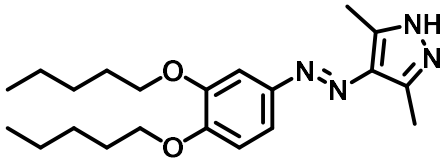
The corresponding dione (1.0 eq.) was dissolved in ethanol (10 mL/mmol) and hydrazine (1.0 eq.) was added. The solution was refluxed overnight. The crude product was extracted with DCM (2x 30 mL) and washed with H_2O (2x 30 mL) and brine (1x 30 mL). The organic layer was dried with $MgSO_4$, and the solvent was removed. The crude product was purified by column chromatography (silica, CH:EtOAc 10:1). The product was received as yellow solid.

(E)-4-((3,4-dimethoxyphenyl)diazenyl)-3,5-dimethyl-1H-pyrazole (2d)



Yield: 1.22 g (94%). **1H-NMR** (400 MHz, CDCl3): δ = 7.51 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.42 (dd, *J* = 11.9, 2.2 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 3.97 (dd, *J* = 5.5, 1.7 Hz, 6H), 2.65 (s, 6H). ppm. **13C-NMR** (100 MHz, CDCl3): δ = 151.26, 149.68, 147.74, 140.75, 134.32, 119.90, 119.02, 110.64, 101.89, 56.29, 56.26, 56.07, 56.03, 12.01 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{13}H_{16}N_4O_2Na]^+$: 283.11655; found 283.11640 [M+Na]+.

(E)-4-((3,4-bis(pentyloxy)phenyl)diazenyl)-3,5-dimethyl-1H-pyrazole (2e)



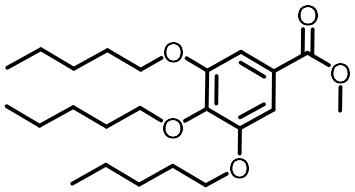
Yield: 389 mg (74%). **1H-NMR** (400 MHz, CDCl3): δ = 7.49 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.39 (dd, *J* = 17.0, 2.3 Hz, 1H), 6.96 (dd, *J* = 8.6, 2.5 Hz, 1H), 4.12 – 4.03 (m, 4H), 2.79 (s, 3H), 2.58 – 2.46 (m, 3H), 1.93 – 1.83 (m, 4H), 1.53 – 1.37 (m, 8H), 0.99 – 0.90 (m, 6H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 152.69, 152.02, 150.28, 149.76, 149.71, 147.67, 147.41, 147.06, 144.42, 140.04, 137.90, 133.60, 120.36, 119.57, 113.63, 113.25, 112.53, 112.29, 104.24, 103.78, 70.90, 70.61, 69.41, 69.37, 69.32, 29.00, 28.96, 28.40, 28.39, 28.34, 28.33, 28.21, 28.04, 22.63, 22.61, 22.49, 22.40, 15.19, 14.19, 14.18, 14.12, 14.07, 11.60, 11.55, 11.02, 9.52 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{21}H_{32}N_4O_2Na]^+$: 395.24175; found 395.24171 [M+Na]+.

Synthesis of Precursors for 3b-d

General Procedure V: Synthesis of methyl 3,4,5-tris(alkloxy)benzoate [1]

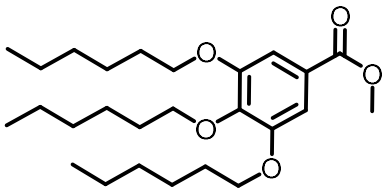
Gallic acid methyl ester (1.0 eq.) was dissolved in DMF (5 mL/mmol) under argon and K_2CO_3 (7.5 eq.) and the corresponding bromo alkane (5.0 eq.) were added. The mixture was stirred at 80 °C overnight. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, CH/EtOAc 10:1). The product was received as white solid.

methyl 3,4,5-tris(pentyloxy)benzoate (31b)



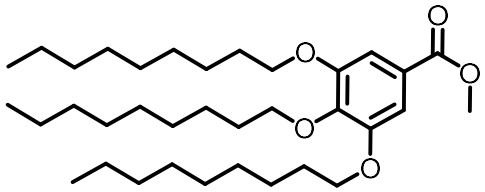
Yield: 3.92 g (99%). **1H-NMR** (400 MHz, CDCl3): δ = 7.25 (s, 2H), 4.01 (td, *J* = 6.5, 3.0 Hz, 6H), 3.89 (s, 3H), 1.85 – 1.73 (m, 6H), 1.41 (ddt, *J* = 28.6, 14.2, 6.9 Hz, 12H), 0.92 (td, *J* = 7.2, 4.2 Hz, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 167.09, 152.98, 142.53, 124.82, 108.15, 73.59, 69.32, 53.56, 52.24, 30.12, 29.13, 28.38, 28.35, 28.32, 22.67, 22.57, 14.20, 14.16 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{23}H_{38}O_5Na]^+$: 417.26115; found 417.26119 [M+Na]+.

methyl 3,4,5-tris(hexyloxy)benzoate (31c)



Yield: 4.19 g (96%). **1H-NMR** (400 MHz, CDCl3): δ = 7.25 (s, 2H), 4.01 (td, *J* = 6.6, 2.7 Hz, 6H), 3.89 (s, 3H), 1.85 – 1.71 (m, 6H), 1.48 (p, *J* = 6.8 Hz, 6H), 1.36 – 1.30 (m, 12H), 0.92 – 0.88 (m, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 167.10, 152.97, 142.53, 124.81, 108.14, 73.63, 69.32, 52.24, 31.87, 31.70, 30.42, 29.41, 25.89, 25.84, 22.81, 22.76, 14.21, 14.16 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{26}H_{44}O_5Na]^+$: 459.30810; found 459.30812 [M+Na]+.

methyl 3,4,5-tris(nonyloxy)benzoate (31d)

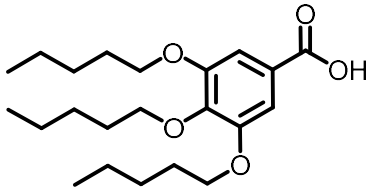


Yield: 4.57 g (81%). **1H-NMR** (400 MHz, CDCl3): δ = 7.25 (s, 2H), 4.01 (td, *J* = 6.6, 2.9 Hz, 6H), 3.89 (s, 3H), 1.83 – 1.72 (m, 6H), 1.47 (p, *J* = 6.9 Hz, 6H), 1.37 – 1.28 (m, 30H), 0.92 – 0.84 (m, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 167.10, 161.35, 152.97, 142.54, 124.80, 108.15, 73.64, 69.33, 64.28, 52.24, 34.19, 33.00, 32.09, 32.05, 31.99, 30.48, 29.82, 29.73, 29.72, 29.54, 29.51, 29.46, 29.44, 29.35, 26.23, 26.20, 25.96, 22.84, 22.83, 22.80, 14.25 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{35}H_{62}O_5Na]$+: 585.44895; found 585.44853 [M+Na]+.

General Procedure VI: Deprotection of 3,4,5-tris(alkoxy)benzoic acid [1]

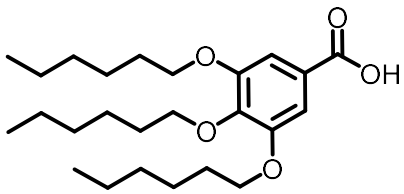
Product of procedure V (1.0 eq.) was dissolved in EtOH (3 mL/mmol) and aq. Solution of KOH (6 eq.) was added to the mixture. The solution was stirred at 100 °C for 5 h. The resulting mixture was cooled down and poured in an ice-cooled solution of concentrated HCl (10 mL) in H_2O (200 mL). The occurring precipitate was filtered and washed with H_2O. The product was received without further purification as a white solid.

3,4,5-tris(pentyloxy)benzoic acid (32b)



Yield: 3.78 g (97%). **1H-NMR** (400 MHz, CDCl3): δ = 7.32 (s, 2H), 4.06 – 4.01 (m, 6H), 1.87 – 1.73 (m, 6H), 1.51 – 1.35 (m, 12H), 0.93 (td, *J* = 7.2, 4.2 Hz, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 171.13, 153.03, 143.33, 123.66, 108.74, 73.67, 69.36, 30.13, 29.11, 28.38, 28.32, 22.67, 22.58, 14.22, 14.17 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{22}H_{35}O_5]$-: 379.24790; found 379.24829 [M-H]-.

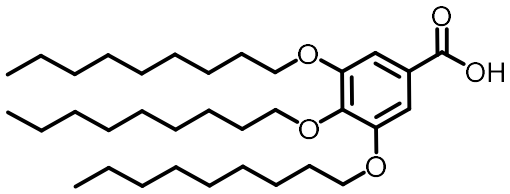
3,4,5-tris(hexyloxy)benzoic acid (32c)



Yield: 3.16 g (78%). **1H-NMR** (400 MHz, CDCl3): δ = 7.31 (s, 2H), 4.03 (dt, *J* = 8.9, 6.5 Hz, 6H), 1.83 – 1.73 (m, 6H), 1.50 – 1.44 (m, 6H), 1.36 – 1.31 (m, 12H), 0.93 – 0.89 (m, 9H) ppm.

13C-NMR (100 MHz, CDCl3): δ = 171.41, 152.98, 143.11, 124.23, 108.67, 73.69, 69.33, 31.87, 31.71, 30.43, 29.41, 25.90, 25.84, 22.82, 22.77, 14.22, 14.16 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{25}H_{41}O_5]$-: 421.29595; found 421.29526 [M-H]-.

3,4,5-tris(nonyloxy)benzoic acid (32d)

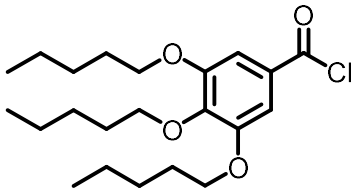


Yield: 3.21 g (72%). **1H-NMR** (400 MHz, CDCl3): δ = 7.18 (s, 2H), 3.93 (dt, *J* = 19.2, 6.5 Hz, 6H), 1.72 (p, *J* = 6.6 Hz, 6H), 1.47 – 1.37 (m, 6H), 1.29 – 1.26 (m, 30H), 0.92 – 0.83 (m, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 152.81, 108.21, 73.57, 69.21, 63.26, 32.97, 32.11, 32.09, 32.03, 30.57, 29.87, 29.80, 29.70, 29.60, 29.56, 29.51, 29.41, 26.36, 26.27, 25.89, 22.85, 22.82, 14.25 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{34}H_{59}O_5]$-: 547.43680; found 547.43628 [M-H]-.

General Procedure VII: 3,4,5-tris(alkoxy)benzoyl chloride [1]

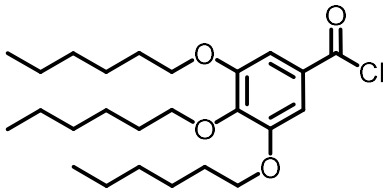
Product of procedure VI (1.0 eq.) was dissolved in dry DCM (5 mL/mmol) and thionyl chloride (8 eq.) was added dropwise. The solution was stirred at room temperature overnight. The solvent and remaining thionyl chloride were removed by vacuum distillation. The product was received as light-yellow oil and used without further purification.

3,4,5-tris(pentyloxy)benzoyl chloride (33b)



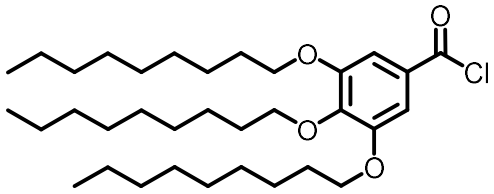
Yield: 3.82 g (100%). **1H-NMR** (400 MHz, CDCl3): δ = 7.33 (s, 2H), 4.10 – 4.01 (m, 6H), 1.87 – 1.72 (m, 6H), 1.51 – 1.33 (m, 12H), 0.96 – 0.91 (m, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 167.88, 153.04, 144.94, 127.45, 110.19, 77.48, 76.84, 73.86, 69.53, 30.13, 29.03, 28.35, 28.25, 22.63, 22.55, 14.20, 14.15 ppm.

3,4,5-tris(hexyloxy)benzoyl chloride (33c)



Yield: 3.30 g (100%). **1H-NMR** (400 MHz, CDCl3): δ = 7.33 (s, 2H), 4.10 – 4.01 (m, 6H), 1.86 – 1.71 (m, 6H), 1.52 – 1.44 (m, 6H), 1.37 – 1.30 (m, 12H), 0.93 – 0.89 (m, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 167.87, 153.03, 144.94, 127.44, 110.19, 73.89, 69.53, 31.82, 31.67, 30.42, 29.31, 25.86, 25.77, 22.80, 22.74, 14.20, 14.15 ppm.

3,4,5-tris(nonyloxy)benzoyl chloride (33d)

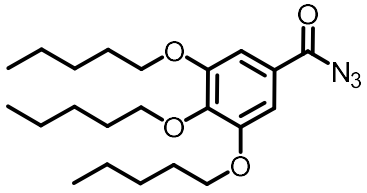


Yield: 3.32 g (100%). **1H-NMR** (400 MHz, CDCl3): δ = 7.33 (s, 2H), 4.10 – 4.00 (m, 6H), 1.84 – 1.72 (m, 6H), 1.51 – 1.43 (m, 6H), 1.35 – 1.28 (m, 30H), 0.90 – 0.87 (m, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 167.87, 153.03, 144.95, 127.43, 110.20, 73.89, 69.54, 67.82, 62.51, 32.08, 32.04, 32.00, 30.48, 29.80, 29.71, 29.67, 29.52, 29.50, 29.42, 29.36, 29.31, 28.87, 26.20, 26.13, 25.91, 25.71, 22.84, 22.83, 22.79, 14.25 ppm.

General Procedure VIII: 3,4,5-tris(alkoxy)benzoyl azide[2]

The Product of procedure VII (1.0 eq.) was dissolved in THF (3 mL/mmol) and added dropwise to an ice-cooled aqueous saturated solution of NaN_3 (15.0 eq.). The solution was stirred for 5 h and the product was extracted with EtOAc (3x 50 mL). The organic layers were combined, washed with water (2x 50 mL) and brine (2x 50 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield the product as a light-brown oil, which could be used without further purification.

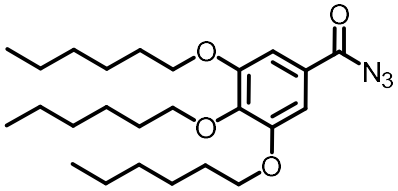
3,4,5-tris(pentyloxy)benzoyl azide (34b)



Yield: 3.68 g (95%). **1H-NMR** (400 MHz, CDCl3): δ = 7.24 (s, 2H), 4.06 – 3.90 (m, 6H), 1.86 – 1.71 (m, 6H), 1.50 – 1.32 (m, 12H), 0.95 – 0.90 (m, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 172.11, 153.11, 143.95, 125.24, 107.96, 73.72, 69.38, 30.13, 29.08, 28.37, 28.29, 22.65,

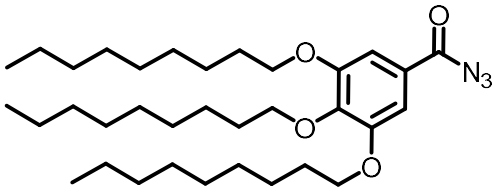
22.57, 14.21, 14.16 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{22}H_{35}N_3O_4Na]^+$: 428.25198; found 428.25175 $[M+Na]^+$.

3,4,5-tris(hexyloxy)benzoyl azide (34c)



Yield: 3.27 g (98%). **1H-NMR** (400 MHz, CDCl3): δ = 7.24 (s, 2H), 4.06 – 3.99 (m, 6H), 1.83 – 1.72 (m, 6H), 1.50 – 1.46 (m, *6*H), 1.37 – 1.30 (m, 12H), 0.92 – 0.88 (m, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 172.10, 153.10, 143.95, 125.23, 107.96, 73.75, 69.39, 31.84, 31.68, 30.42, 29.35, 25.87, 25.80, 22.80, 22.75, 14.20, 14.15 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{25}H_{41}N_3O_4Na]^+$: 442.29278; found 442.29215 $[M+Na]^+$.

3,4,5-tris(nonyloxy)benzoyl azide (34d)

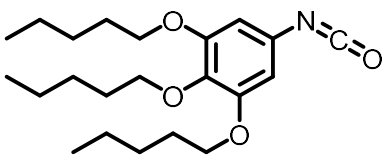


Yield: 3.05 g (91%). **1H-NMR** (400 MHz, CDCl3): δ = 7.24 (s, 2H), 4.06 – 3.99 (m, 6H), 1.85 – 1.70 (m, 6H), 1.51 – 1.43 (m, 6H), 1.34 – 1.27 (m, 30H), 0.90 – 0.87 (m, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 172.11, 153.10, 125.23, 107.98, 73.77, 69.40, 32.09, 32.05, 30.48, 29.81, 29.73, 29.69, 29.53, 29.51, 29.43, 29.41, 26.21, 26.17, 22.83, 14.25 ppm.

General Procedure IX: 1,2,3-tris(alkoxy)-5-isocyanatobenzene[2]

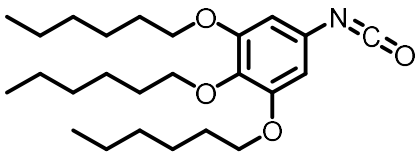
The product of procedure VIII (1.0 eq.) was dissolved in dry toluene (5 mL/mmol) and refluxed under Argon overnight. The solvent was removed under reduced pressure, the product was received as a light-brown oil and used without further purification.

1,2,3-tris(pentyloxy)-5-isocyanatobenzene (35b)



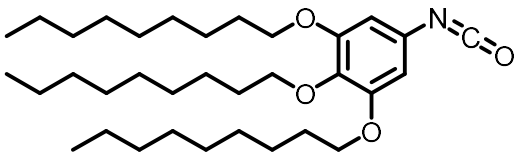
Yield: 3.43 g (100%).

1,2,3-tris(hexyloxy)-5-isocyanatobenzene (35c)



Yield: 3.07 g (100%).

1,2,3-tris(nonyloxy)-5-isocyanatobenzene (35d)

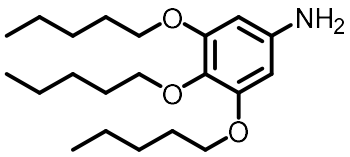


Yield: 2.90 g (100%). **ESI-HRMS** (m/z): Calculated for $[C_{34}H_{59}NO_4Na]+$: 568.43363; found 568.43360 [M+Na]+.

General Procedure X: 3,4,5-tris(alkoxy)aniline[3]

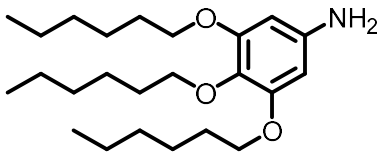
The product of procedure IX was dissolved in 1,4-dioxane (5 mL/mmol) and added dropwise to an aqueous solution of KOH (3M, 20 mL/mmol). The solution was stirred at 90 °C overnight. After cooling down, the developed brown oil was extracted with DCM (3x 30 mL), washed with water (2x 30 mL) and brine (2x 30 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the product was received as a brown oil. In case of not full conversion, the procedure was followed once again, yielding a near complete conversion. The product was used without further purification.

3,4,5-tris(pentyloxy)aniline (36b)



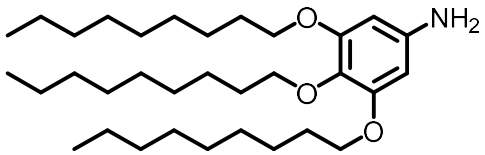
Yield: 3.98 g (quantitative). **1H-NMR** (400 MHz, CDCl3): δ = 5.91 (s, 2H), 3.92 – 3.83 (m, 6H), 1.79 – 1.70 (m, 6H), 1.46 – 1.33 (m, 12H), 0.93 – 0.89 (m, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 153.87, 142.43, 131.28, 94.65, 73.66, 69.12, 67.23, 30.09, 29.24, 28.46, 28.40, 22.74, 22.59, 14.23, 14.18 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{21}H_{37}NO_3Na]+$: 374.26657; found 374.26637 [M+Na]+.

3,4,5-tris(hexyloxy)aniline (36c)



Yield: 3.28 g (quantitative). **1H-NMR** (400 MHz, CDCl3): δ = 5.91 (s, 2H), 3.92 – 3.83 (m, 6H), 1.79 – 1.75 (m, 6H), 1.45 – 1.44 (m, *6*H), 1.34 – 1.30 (m, 12H), 0.91 – 0.88 (m, 9H) ppm. **13C-NMR** (100 MHz, CDCl3): δ = 153.87, 142.45, 131.30, 94.67, 73.73, 69.14, 67.24, 31.96, 31.73, 30.39, 29.53, 25.97, 25.90, 22.84, 22.77, 14.23, 14.17 ppm. **ESI-HRMS** (m/z): Calculated for $[C_{24}H_{43}NO_3Na]+$: 416.31352; found 416.31378 [M+Na]+.

3,4,5-tris(nonyloxy)aniline (36d)



Yield: 2.88 g (quantitative). **ESI-HRMS** (m/z): Calculated for $[C_{33}H_{61}NO_3Na]+$: 542.45437; found 542.45475 [M+Na]+.

X-ray diffraction of AIZ 1a-b, 1d-f and 3a

Data sets for compounds **1a**, **1b**, **1d**, **1e**, **1f** and **3a** were collected with a Bruker D8 Venture Photon III Diffractometer. Programs used: data collection: *APEX4* Version 2021.4-0 [1] (Bruker AXS Inc., **2021**); cell refinement: *SAINT* Version 8.40B (Bruker AXS Inc., **2021**); data reduction: *SAINT* Version 8.40B (Bruker AXS Inc., **2021**); absorption correction, *SADABS* Version 2016/2 (Bruker AXS Inc., **2021**); structure solution *SHELXT*-Version 2018-3 [2] (Sheldrick, G. M. *Acta Cryst.,* **2015**, *A71*, 3-8); structure refinement *SHELXL*- Version 2018-3 [3] (Sheldrick, G. M. *Acta Cryst.,* **2015**, *C71* (1), 3-8) and graphics, *XP* [4] (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). *R*-values are given for observed reflections, and *w*R^2 values are given for all reflections.

Exceptions and special features: For compound **1e** the isoxazole ring and for compound **3a** both entire independent molecules were found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability.

Deposition numbers CCDC-2379009 (for 1a), -2379010 (for 1b), -2379011 (for 1d), -2379012 (for 1e), -2379013 (for 1f) and -2379014 (for 3a) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service via: www.ccdc.cam.ac.uk/data_request/cif

X-ray crystal structure analysis of 1a (rav10462)

A yellow, prism-like specimen of C13H15N3O3, approximate dimensions 0.078 mm x 0.148 mm x 0.293 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1605 frames were collected. The total exposure time was 8.62 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 8662 reflections to a maximum θ angle of 66.61° (0.84 Å resolution), of which 2310 were independent (average redundancy 3.750, completeness = 98.9%, Rint = 3.04%, Rsig = 3.34%) and 2127 (92.08%) were greater than 2σ(F2). The final cell constants of a = 8.6305(2) Å, b = 8.7260(2) Å, c = 8.8201(2) Å, α = 95.4050(10)°, β = 94.0280(10)°, γ = 91.9550(10)°, volume = 659.10(3) Å3, are based upon the refinement of the XYZ-centroids of 6268 reflections above 20 σ(I) with 10.10° < 2θ < 133.1°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.870. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8010 and 0.9410. 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, C13H15N3O3. The final anisotropic full-matrix least-squares refinement on F2 with 176 variables converged at R1 = 3.62%, for the observed data and wR2 = 9.81% for all data. The goodness-of-fit was 1.068. The largest peak in the final difference electron density synthesis was 0.195 e-/Å3 and the largest hole was -0.272 e-/Å3 with an RMS deviation of 0.044 e-/Å3. On the basis of the final model, the calculated density was 1.317 g/cm3 and F(000), 276 e-. CCDC Nr.: 2379009.

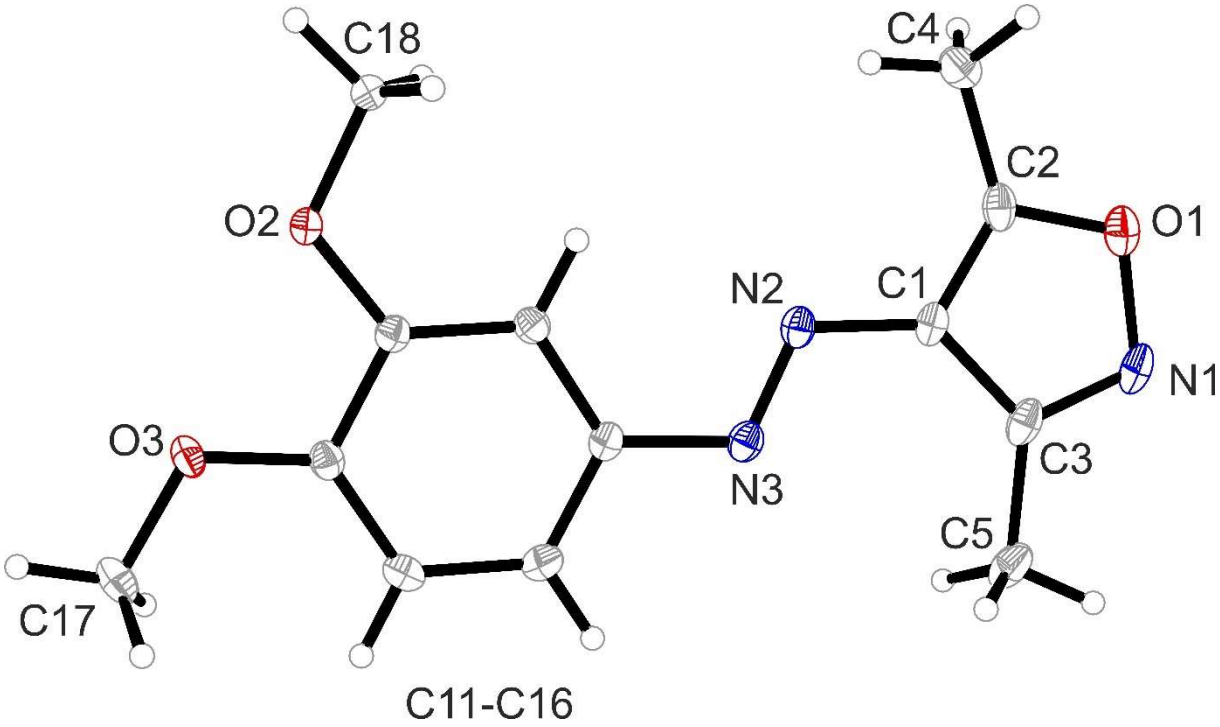


Figure S20. Triclinic crystal structure of AIZ **1a**. Thermal ellipsoids are shown at 50% probability.

X-ray crystal structure analysis of 1b (rav10525)

A yellow, needle-like specimen of $C_{13}H_{15}N_3O_3$, approximate dimensions 0.038 mm x 0.067 mm x 0.138 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1042 frames were collected. The total exposure time was 12.28 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 9508 reflections to a maximum θ angle of 66.52° (0.84 Å resolution), of which 2296 were independent (average redundancy 4.141, completeness = 99.3%, R_{int} = 10.10%, R_{sig} = 7.20%) and 1470 (64.02%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.3236(3) Å, b = 8.5662(3) Å, c = 12.2670(5) Å, α = 96.100(3)°, β = 105.945(3)°, γ = 114.141(3)°, volume = 653.96(5) $Å^3$, are based upon the refinement of the XYZ-centroids of 2344 reflections above 20 σ(I) with 7.739° < 2θ < 132.7°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent

transmission was 0.841. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8980 and 0.9700. 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, $C_{13}H_{15}N_3O_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 176 variables converged at R1 = 5.37%, for the observed data and wR2 = 14.99% for all data. The goodness-of-fit was 1.025. The largest peak in the final difference electron density synthesis was 0.237 $e^-/Å^3$ and the largest hole was -0.239 $e^-/Å^3$ with an RMS deviation of 0.059 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.327 g/cm^3 and F(000), 276 e^-. CCDC Nr.: 2379010.

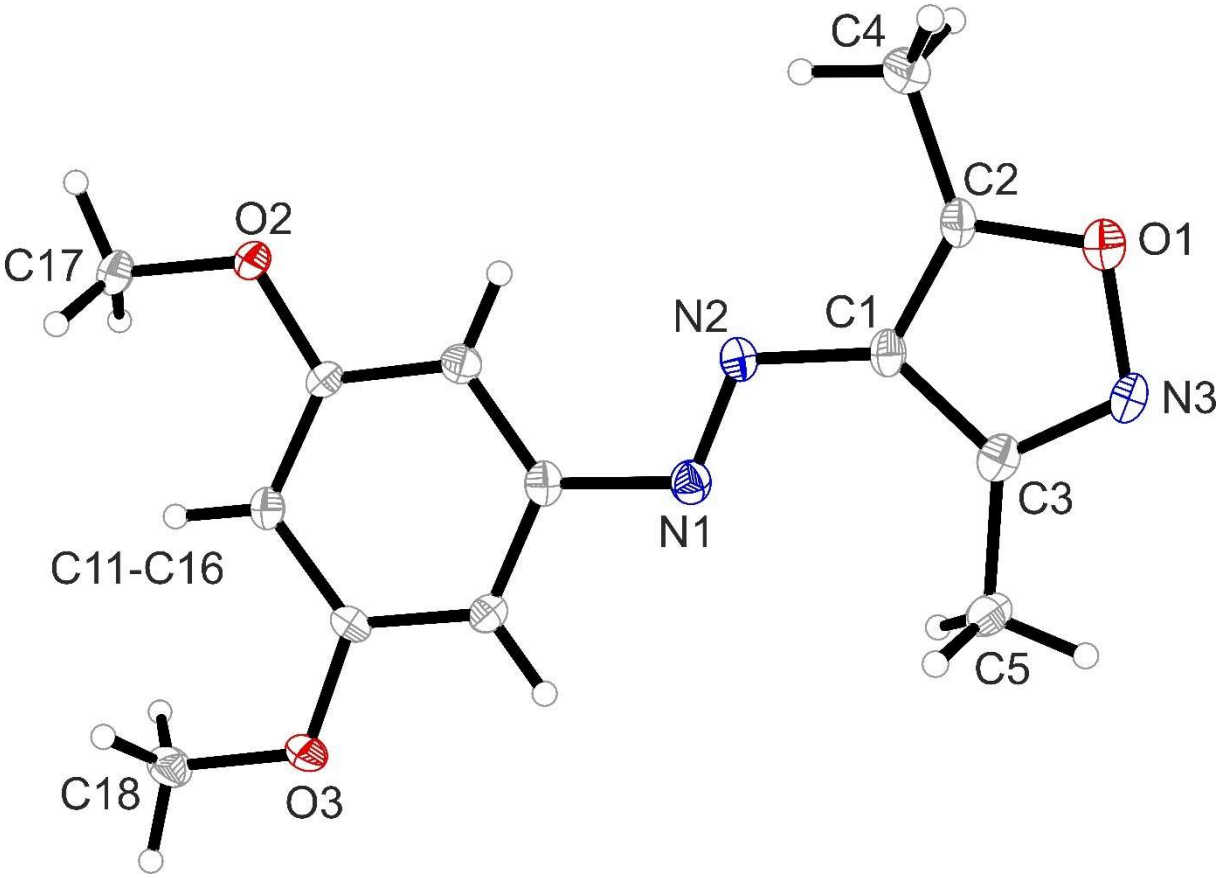


Figure S21. Triclinic crystal structure of AIZ **1b**. Thermal ellipsoids are shown at 50% probability.

X-ray crystal structure analysis of 1d (rav10539)

A yellow, needle-like specimen of $C_{13}H_{15}N_3O_3$, approximate dimensions 0.043 mm x 0.057 mm x 0.436 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1516 frames were collected. The total exposure time was 23.73 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 15605 reflections to a maximum θ angle of 66.74° (0.84 Å resolution), of which 2218 were

independent (average redundancy 7.036, completeness = 98.9%, R_{int} = 20.95%, R_{sig} = 9.39%) and 1247 (56.22%) were greater than $2\sigma(F^2)$. The final cell constants of a = 4.9759(4) Å, b = 33.170(3) Å, c = 7.8476(7) Å, β = 101.454(7)°, volume = 1269.46(19) $Å^3$, are based upon the refinement of the XYZ-centroids of 1144 reflections above 20 σ(I) with 10.66° < 2θ < 132.0°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.677. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7160 and 0.9660. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{13}H_{15}N_3O_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 177 variables converged at R1 = 9.49%, for the observed data and wR2 = 28.08% for all data. The goodness-of-fit was 1.031. The largest peak in the final difference electron density synthesis was 0.516 $e^-/Å^3$ and the largest hole was -0.421 $e^-/Å^3$ with an RMS deviation of 0.141 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.367 g/cm^3 and F(000), 552 e^-. CCDC Nr.: 2379011.

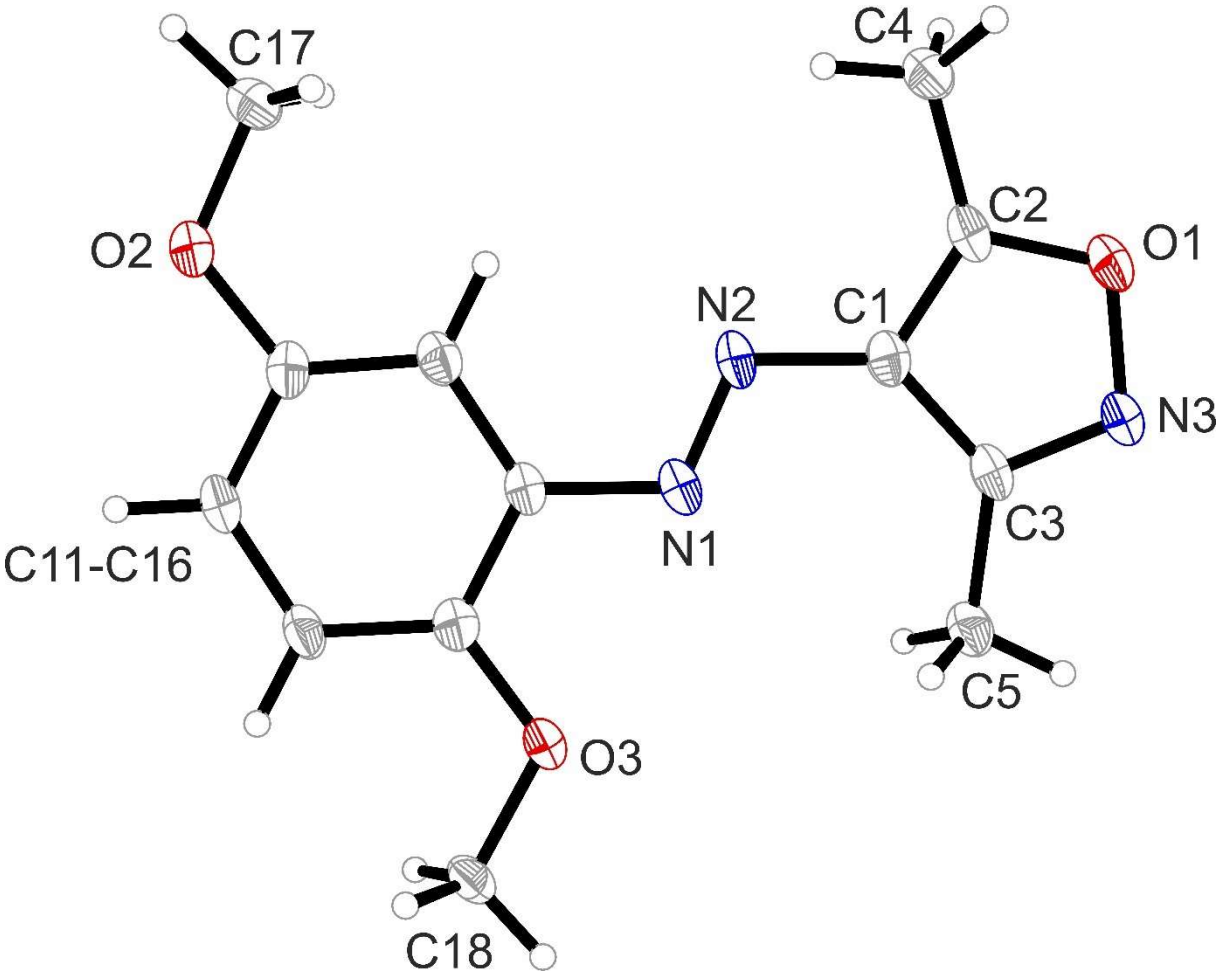


Figure S22. Monoclinic crystal structure of AIZ **1d**. Thermal ellipsoids are shown at 30% probability.

X-ray crystal structure analysis of 1e (rav10540)

A yellow, needle-like specimen of $C_{13}H_{15}N_3O_3$, approximate dimensions 0.043 mm x 0.057 mm x 0.436 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1516 frames were collected. The total exposure time was 23.73 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 15605 reflections to a maximum θ angle of 66.74° (0.84 Å resolution), of which 2218 were independent (average redundancy 7.036, completeness = 98.9%, R_{int} = 20.95%, R_{sig} = 9.39%) and 1247 (56.22%) were greater than $2\sigma(F^2)$. The final cell constants of a = 4.9759(4) Å, b = 33.170(3) Å, c = 7.8476(7) Å, β = 101.454(7)°, volume = 1269.46(19) $Å^3$, are based upon the refinement of the XYZ-centroids of 1144 reflections above 20 σ(I) with 10.66° < 2θ < 132.0°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.677. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7160 and 0.9660. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{13}H_{15}N_3O_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 177 variables converged at R1 = 9.49%, for the observed data and wR2 = 28.08% for all data. The goodness-of-fit was 1.031. The largest peak in the final difference electron density synthesis was 0.516 $e^-/Å^3$ and the largest hole was -0.421 $e^-/Å^3$ with an RMS deviation of 0.141 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.367 g/cm^3 and F(000), 552 e^-. CCDC Nr.: 2379012.

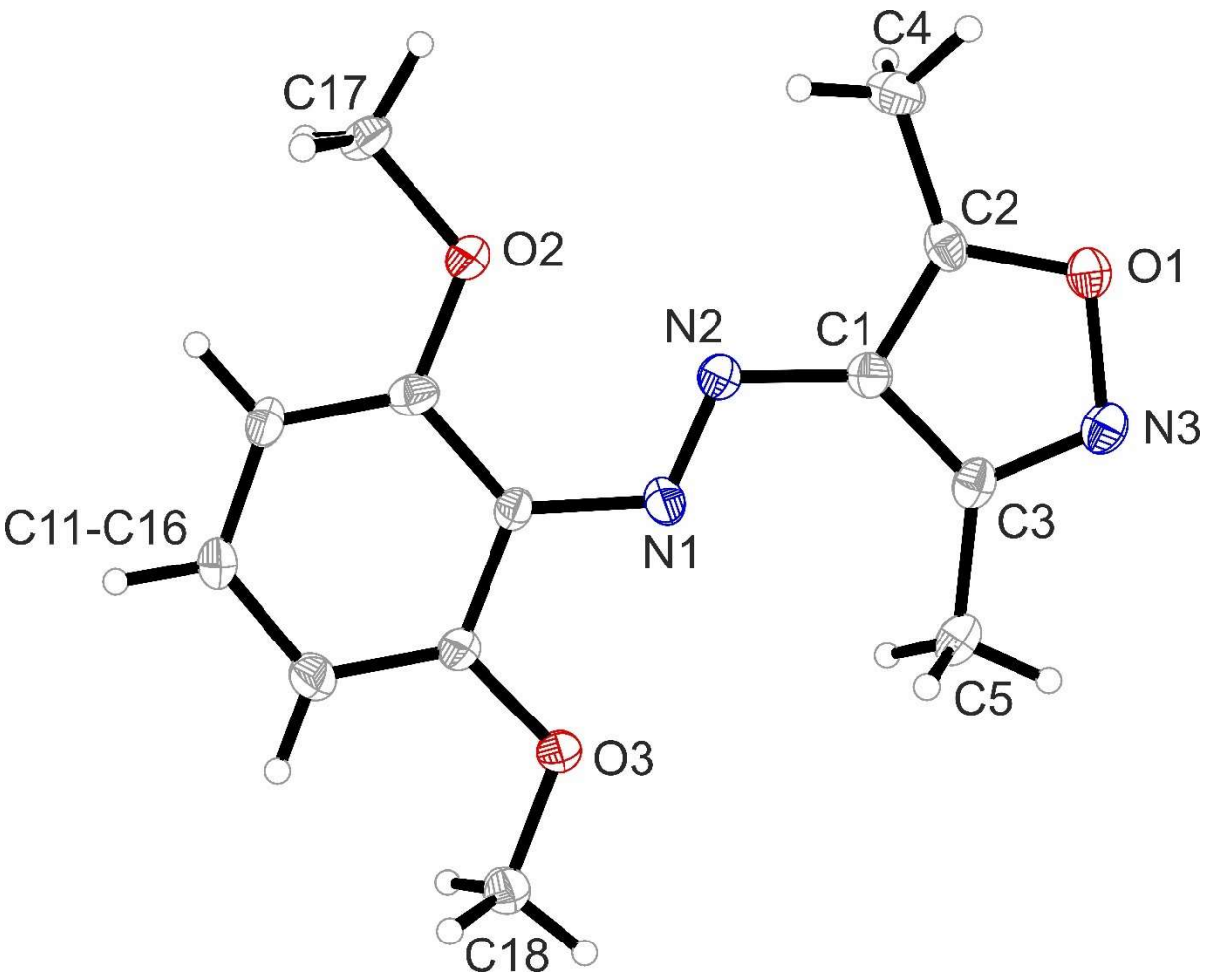


Figure S23. Triclinic crystal structure of AIZ **1e**. Thermal ellipsoids are shown at 50% probability.

X-ray crystal structure analysis of 1f (rav10549)

A yellow, needle-like specimen of $C_{13}H_{15}N_3O_3$, approximate dimensions 0.050 mm x 0.067 mm x 0.201 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1763 frames were collected. The total exposure time was 24.30 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 24621 reflections to a maximum θ angle of 66.71° (0.84 Å resolution), of which 2257 were independent (average redundancy 10.909, completeness = 99.8%, R_{int} = 9.96%, R_{sig} = 3.74%) and 1667 (73.86%) were greater than $2\sigma(F^2)$. The final cell constants of a = 4.7953(2) Å, b = 16.4684(6) Å, c = 16.2760(7) Å, β = 97.511(3)°, volume = 1274.30(9) $Å^3$, are based upon the refinement of the XYZ-centroids of 4579 reflections above 20 σ(I) with 7.670° < 2θ < 133.4°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.918. The calculated minimum and maximum transmission coefficients (based on crystal

size) are 0.8530 and 0.9600. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{13}H_{15}N_3O_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 176 variables converged at R1 = 4.62%, for the observed data and wR2 = 11.78% for all data. The goodness-of-fit was 1.050. The largest peak in the final difference electron density synthesis was 0.193 $e^-/Å^3$ and the largest hole was -0.321 $e^-/Å^3$ with an RMS deviation of 0.054 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.362 g/cm^3 and F(000), 552 e^-. CCDC Nr.: 2379013.

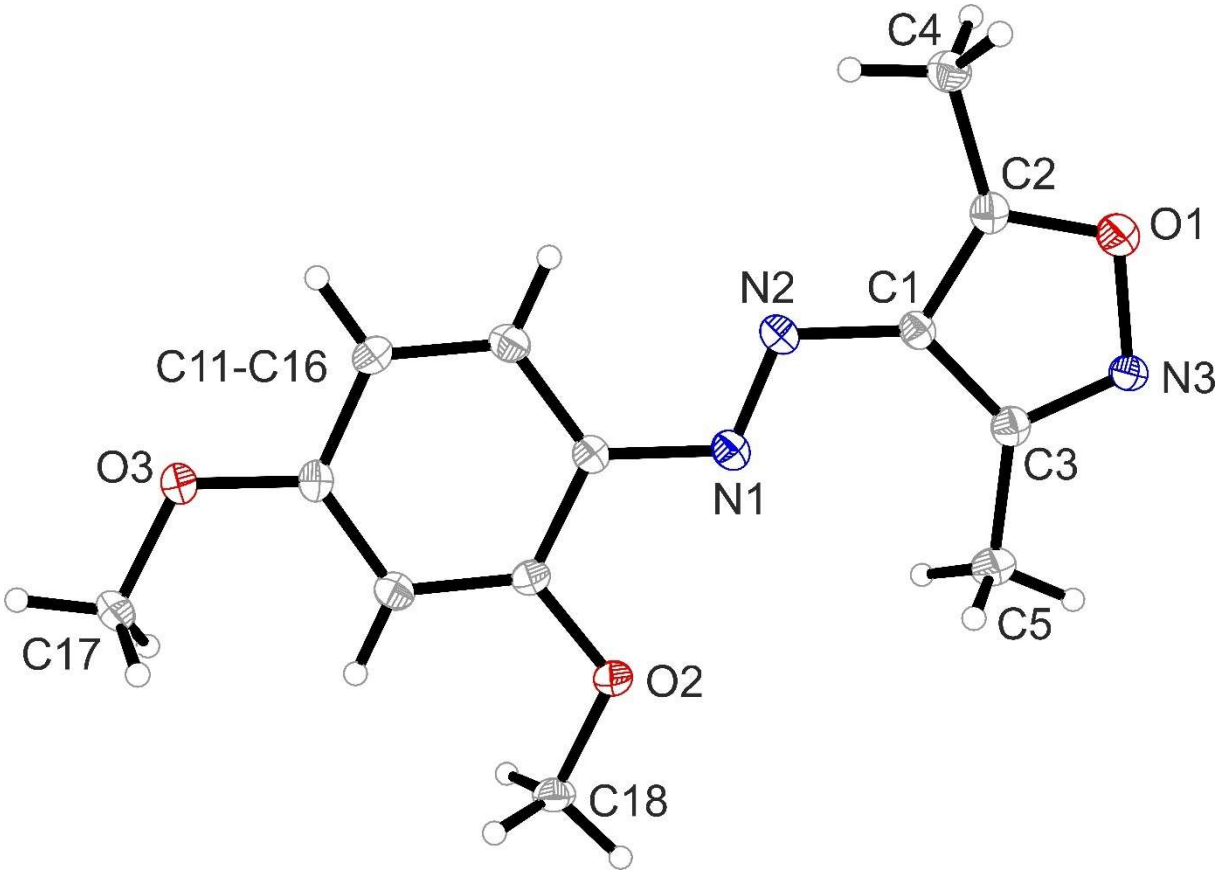


Figure S24. Monoclinic crystal structure of AIZ **1f**. Thermal ellipsoids are shown at 50% probability.

X-ray crystal structure analysis of 3a (rav10512)

A yellow, needle-like specimen of $C_{14}H_{17}N_3O_4$, approximate dimensions 0.046 mm x 0.050 mm x 0.152 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1618 frames were collected. The total exposure time was 21.02 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 25034 reflections to a maximum θ angle of 66.53° (0.84 Å resolution), of which 5067 were independent (average redundancy 4.941, completeness = 99.7%, R_{int} = 12.04%, R_{sig} = 6.94%)

and 3118 (61.54%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.7739(4) Å, b = 12.0725(3) Å, c = 12.6577(3) Å, α = 110.885(2)°, β = 110.484(2)°, γ = 103.357(2)°, volume = 1438.71(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 4381 reflections above 20 σ(I) with 8.499° < 2θ < 132.8°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.860. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8840 and 0.9630. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 4 for the formula unit, $C_{14}H_{17}N_3O_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 773 variables converged at R1 = 5.59%, for the observed data and wR2 = 12.25% for all data. The goodness-of-fit was 1.052. The largest peak in the final difference electron density synthesis was 0.170 $e^-/Å^3$ and the largest hole was -0.193 $e^-/Å^3$ with an RMS deviation of 0.042 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.345 g/cm^3 and F(000), 616 e^-. CCDC Nr.: 2379014.

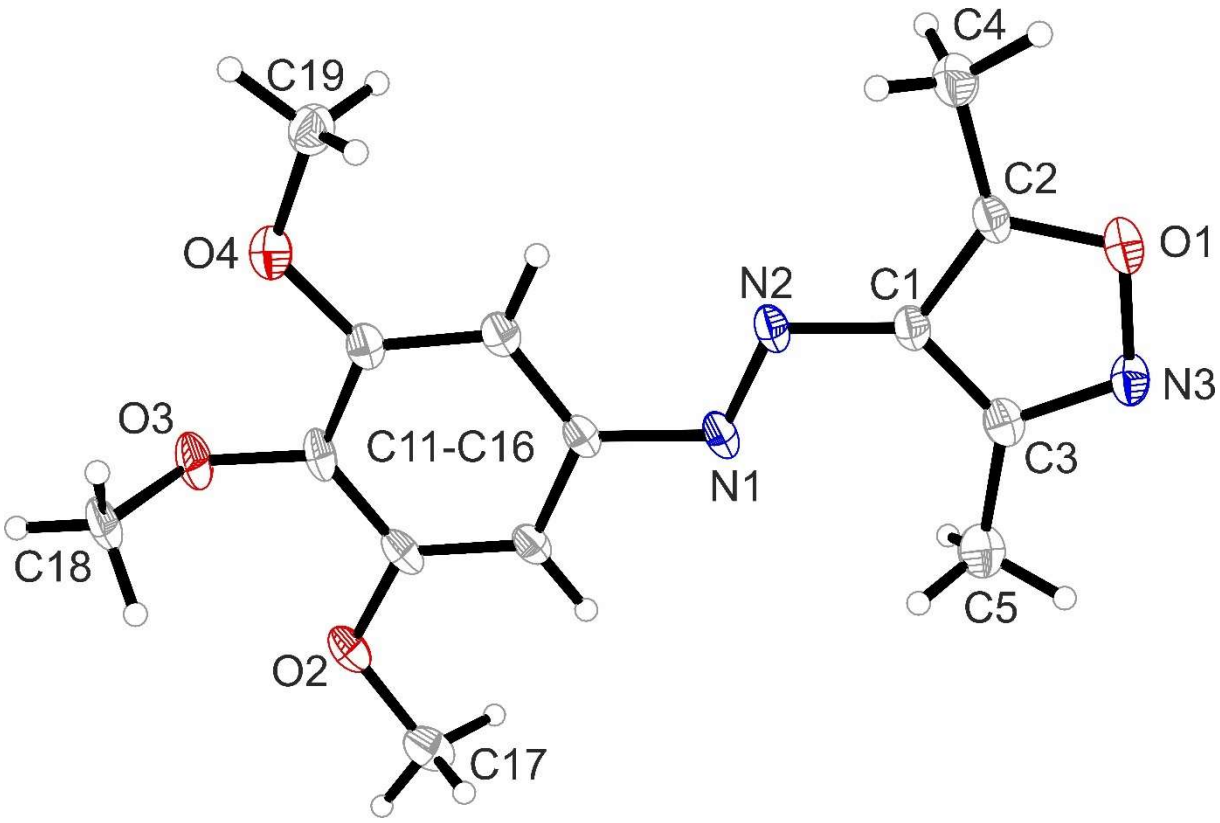


Figure S25. Triclinic crystal structure of AIZ **3a**. Thermal ellipsoids are shown at 30% probability. Only one molecule (molecule named with suffix "A") of two found in the asymmetric unit is shown.

Influence of a second methoxy group on the crystalline packing

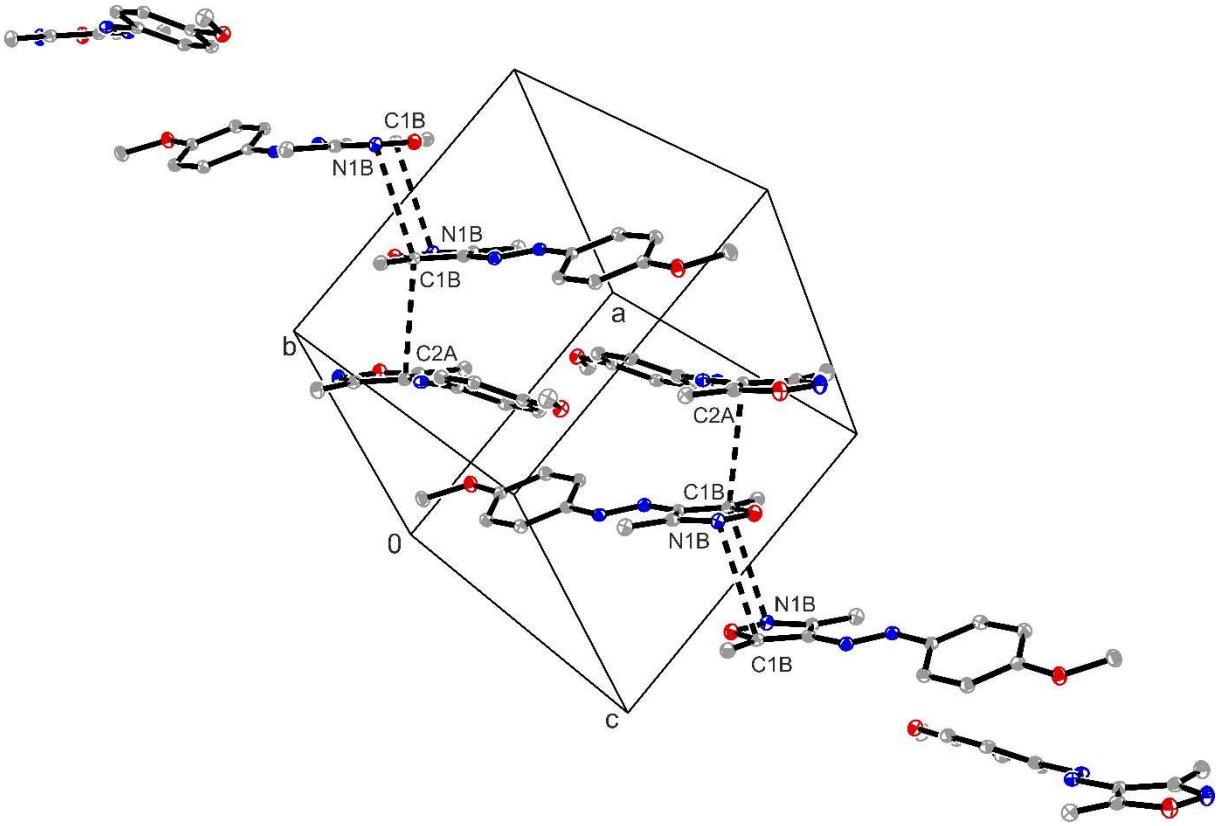


Figure S26. Crystalline packing of the previously published 4-methoxy-AIZ,[11] listed in the Cambridge Crystallographic Data Centre under rav9617

Non-covalent intermolecular π-π interactions between the isoxazole rings of the two molecules (named with suffix A and B) found in the asymmetric unit of the previously published compound 4-methoxy-AIZ:

C1B - N1B 3.296 Å
C1B - C2A 3.470 Å

No intermolecular π-π interactions between the aromatic phenyl rings were observed.
The angle between the two aromatic rings (the phenyl ring and the isoxazole ring) in both molecules are:

24.6° for molecule named with suffix A
24.5° for molecule named with suffix B

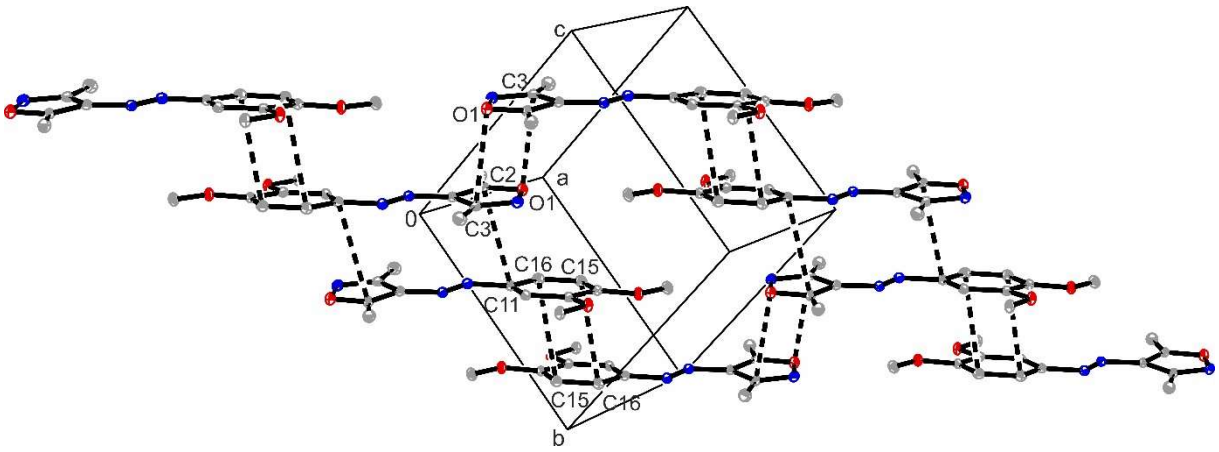


Figure S27. Crystalline packing of the 3,4-dimethoxy-AIZ **1a,** listed in the Cambridge Crystallographic Data Centre under rav10462.

Non-covalent intermolecular π-π interactions between the phenyl-phenyl pairs, phenyl-isoxazole pairs and isoxazole-isoxazole pairs found in the packing diagram of compound **1a**:

C15 - C16 3.483 Å π-π interactions between the phenyl-phenyl pairs
C11 - C2 3.496 Å π-π interactions between the phenyl-isoxazole pairs
C3 - O1 3.276 Å π-π interactions between the isoxazole-isoxazole pairs

The angle between the two aromatic rings (the phenyl ring and the isoxazole ring) in compound **1a** is 5.6°.

Determination of Half-Life Times

The stability of AIZ **1a**, **2a**, **3a** and **3b** and AAP **2e** was determined by measurements at three different temperatures up to 60°C in a solution of the respective compound in acetonitrile with a concentration of c = 50 µmol/L. Through an Eyring plot, the stability at 20°C could be extrapolated.

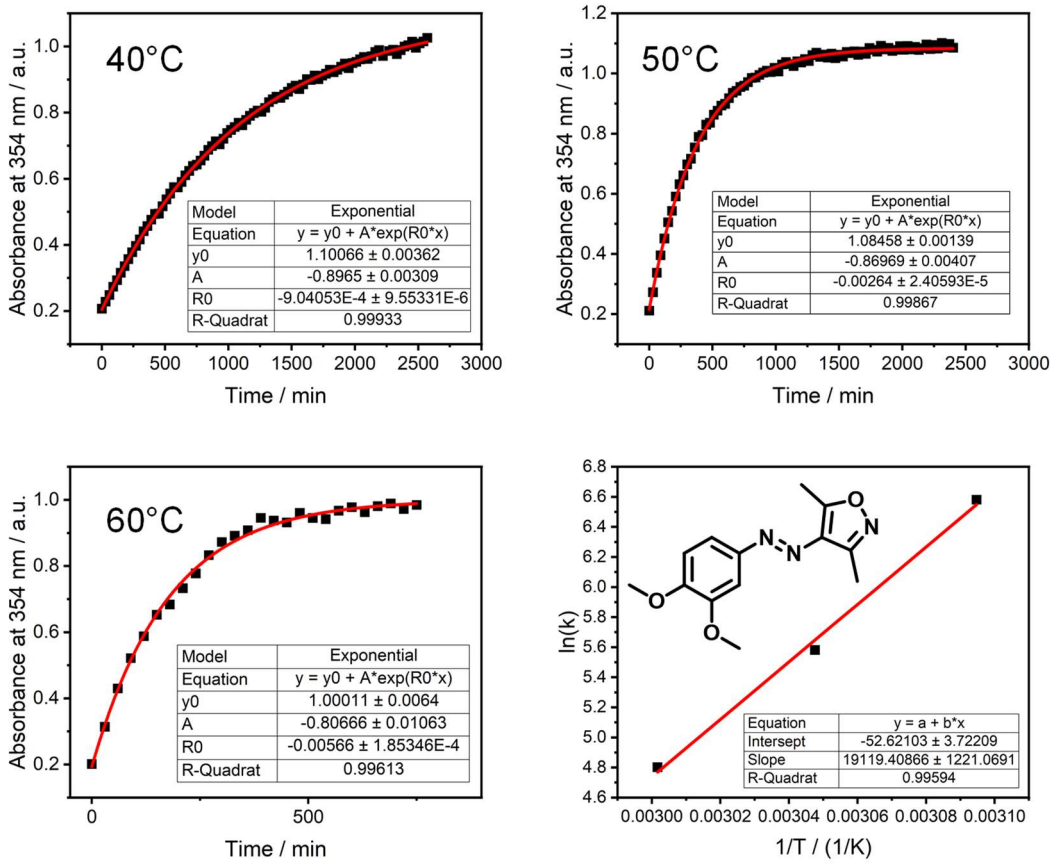


Figure S28. Determination of the half-life of the AIZ **1a** at 40°C, 50°C and 60°C and the Eyring-plot to extrapolate further half-life times.

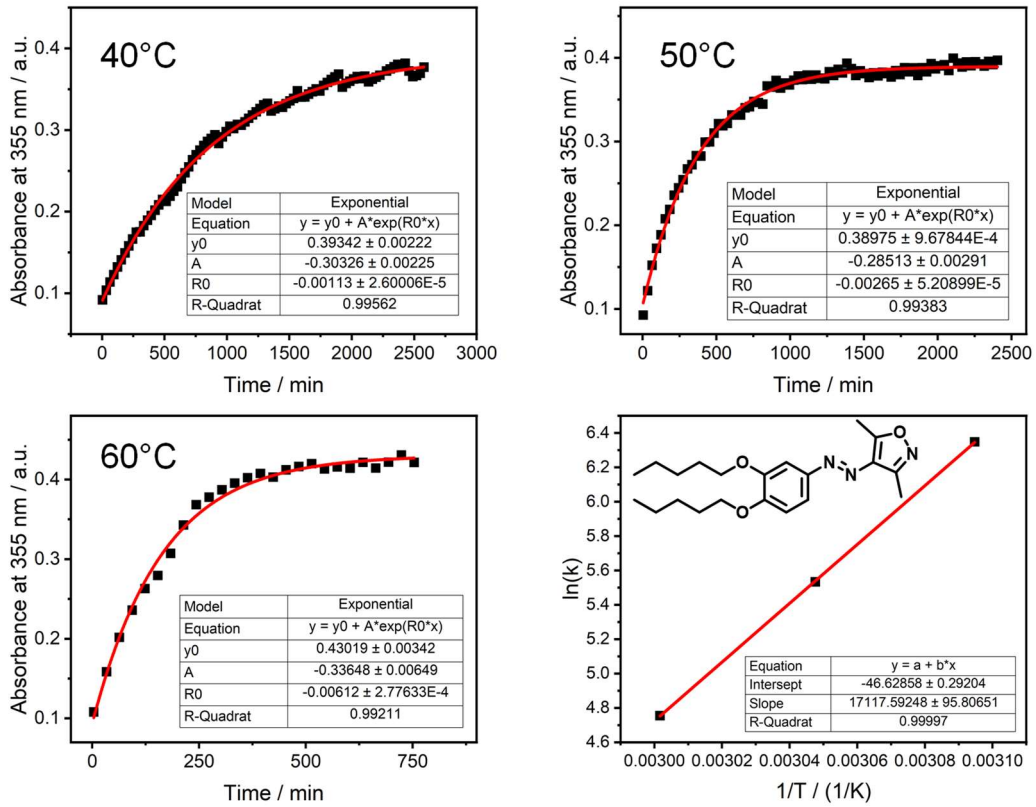


Figure S29. Determination of the half-life of the AIZ **2a** at 40°C, 50°C and 60°C and the Eyring-plot to extrapolate further half-life times.

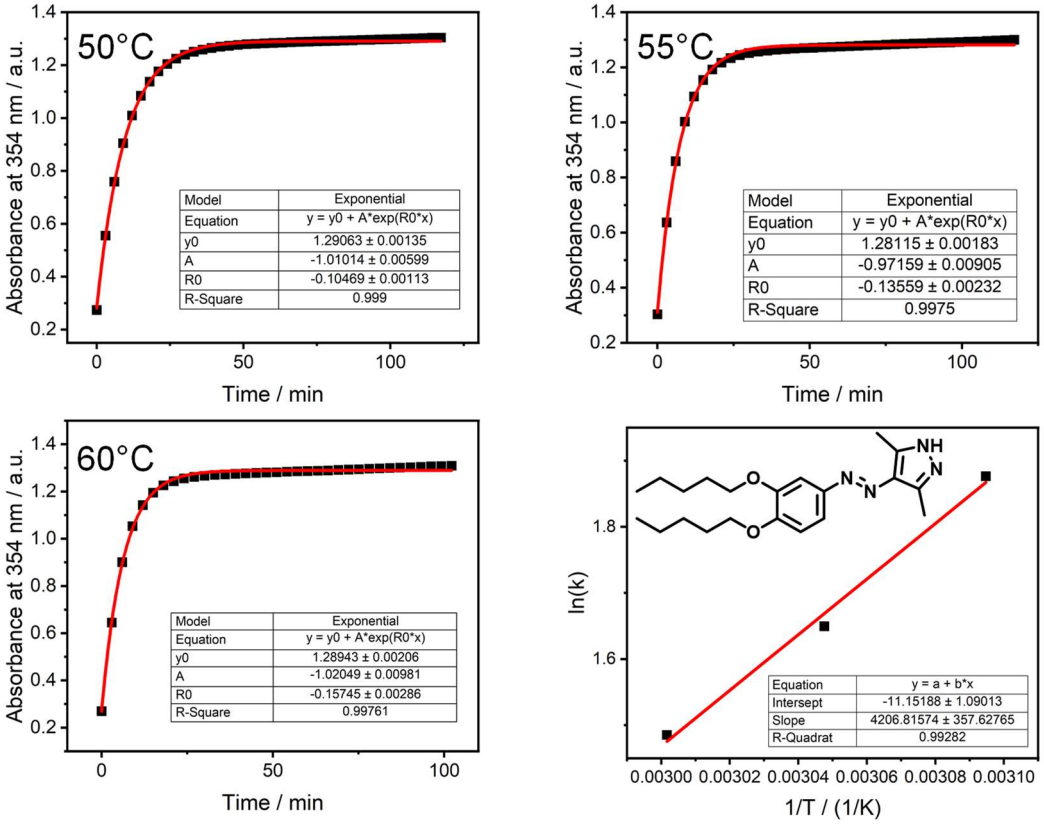


Figure S30. Determination of the half-life of the AAP **2e** at 50°C, 55°C and 60°C and the Eyring-plot to extrapolate further half-life times.

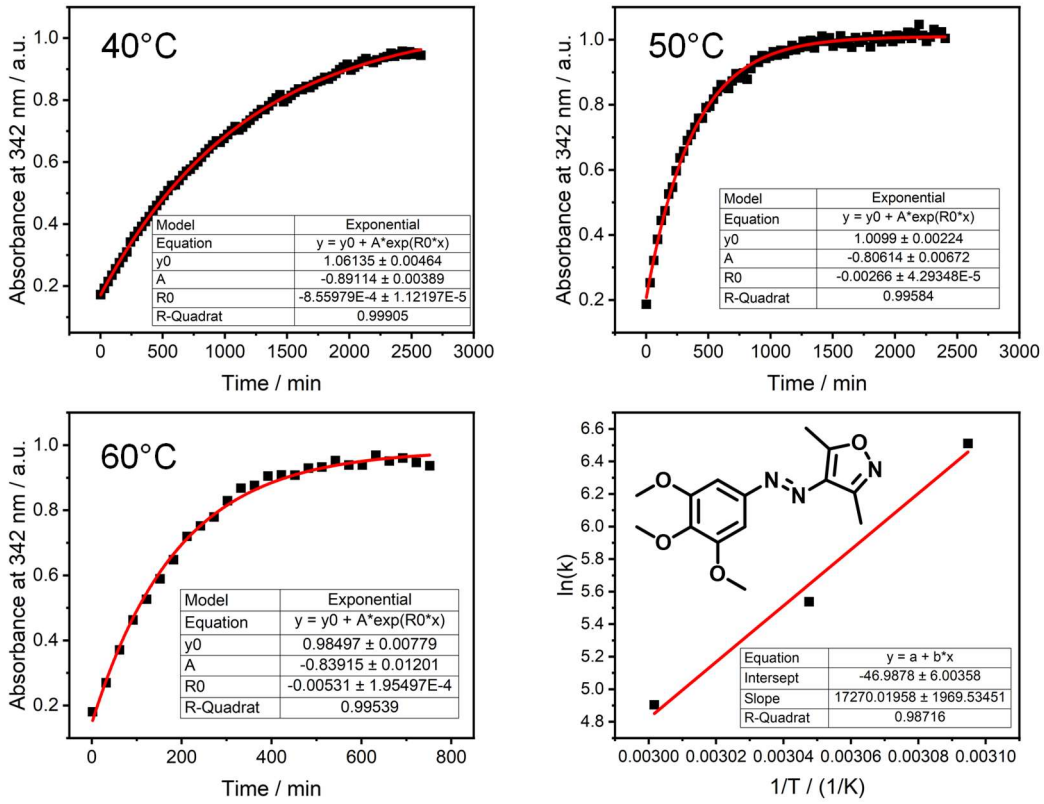


Figure S31. Determination of the half-life of the AIZ **3a** at 40°C, 50°C and 60°C and the Eyring-plot to extrapolate further half-life times.

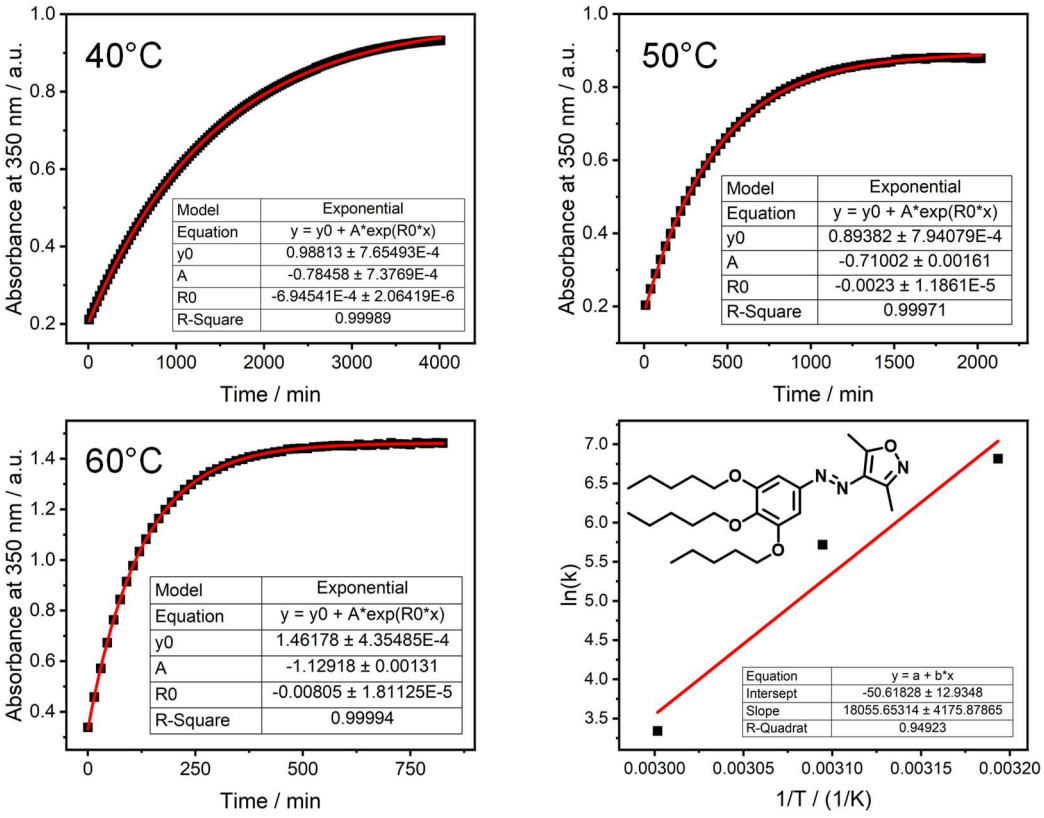


Figure S32. Determination of the half-life of the AIZ **3b** at 40°C, 50°C and 60°C and the Eyring-plot to extrapolate further half-life times.

Differential Scanning Calorimetry (DSC)

The melting points were determined by differential scanning calorimetry on a Netzsch DSC 204 with a fixed scan rate of 5 K min^{-1}.

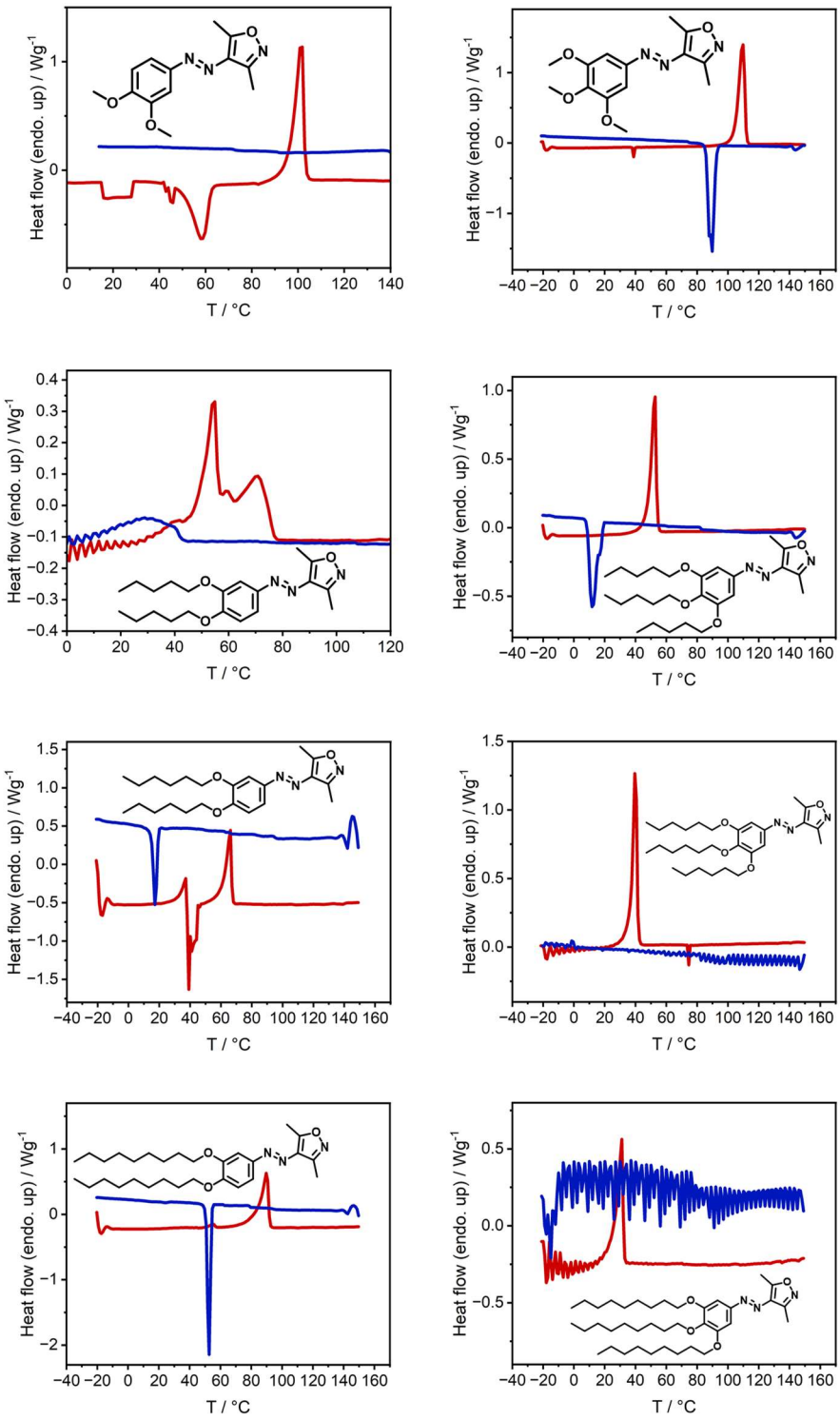


Figure S33. DSC measurements of compounds **1a**, **2a-c**, **3a-d**.

NMR Spectra

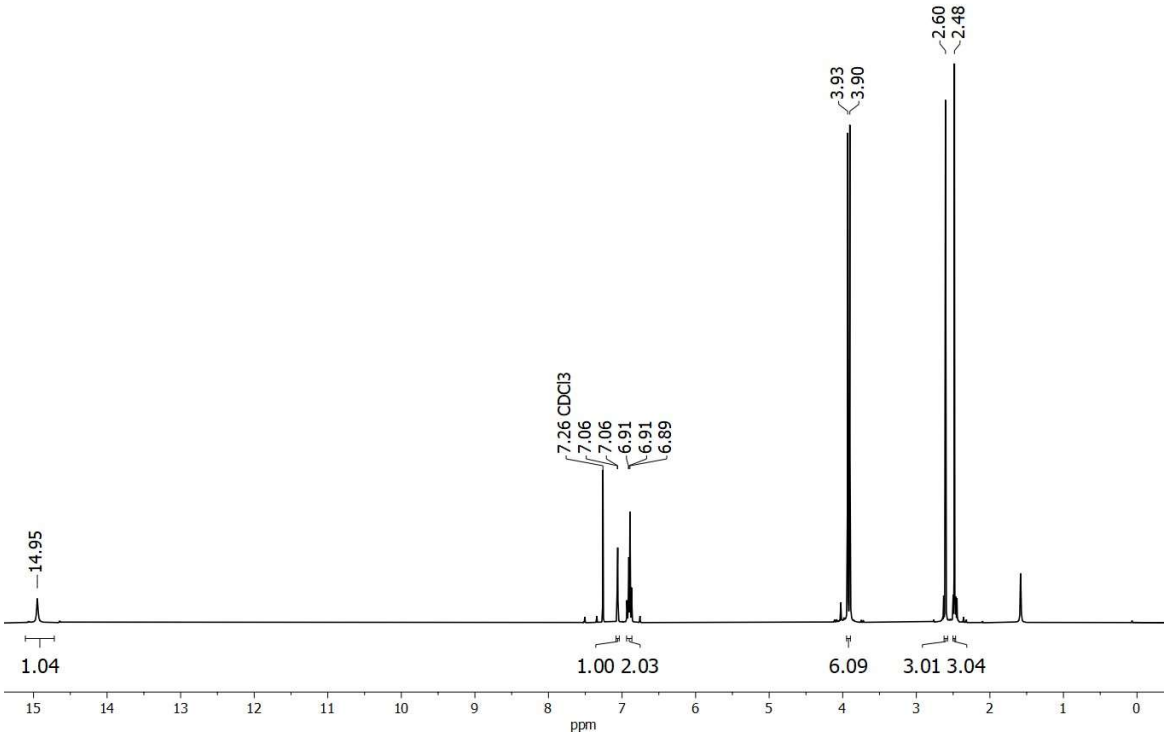


Figure S34. ^{1}H-NMR spectra of compound **11a** dissolved in $CDCl_3$.

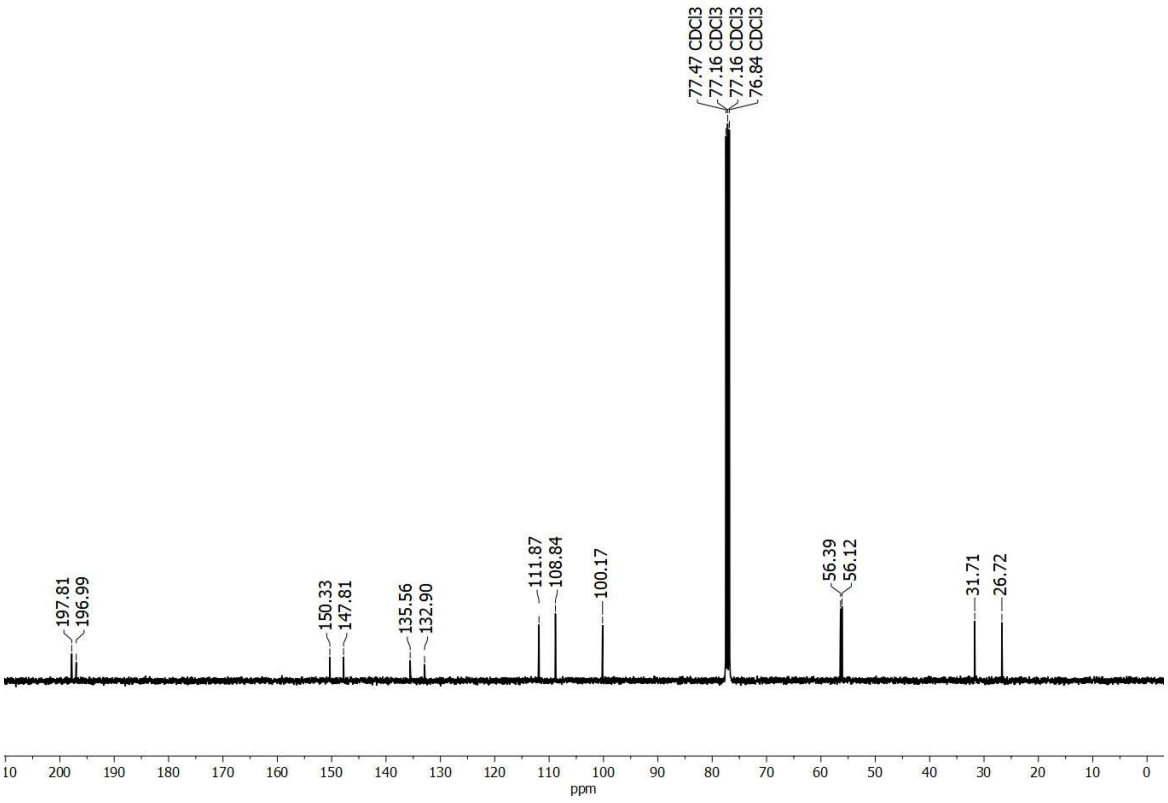


Figure S 35. ^{13}C-NMR spectra of compound **11a** dissolved in $CDCl_3$.

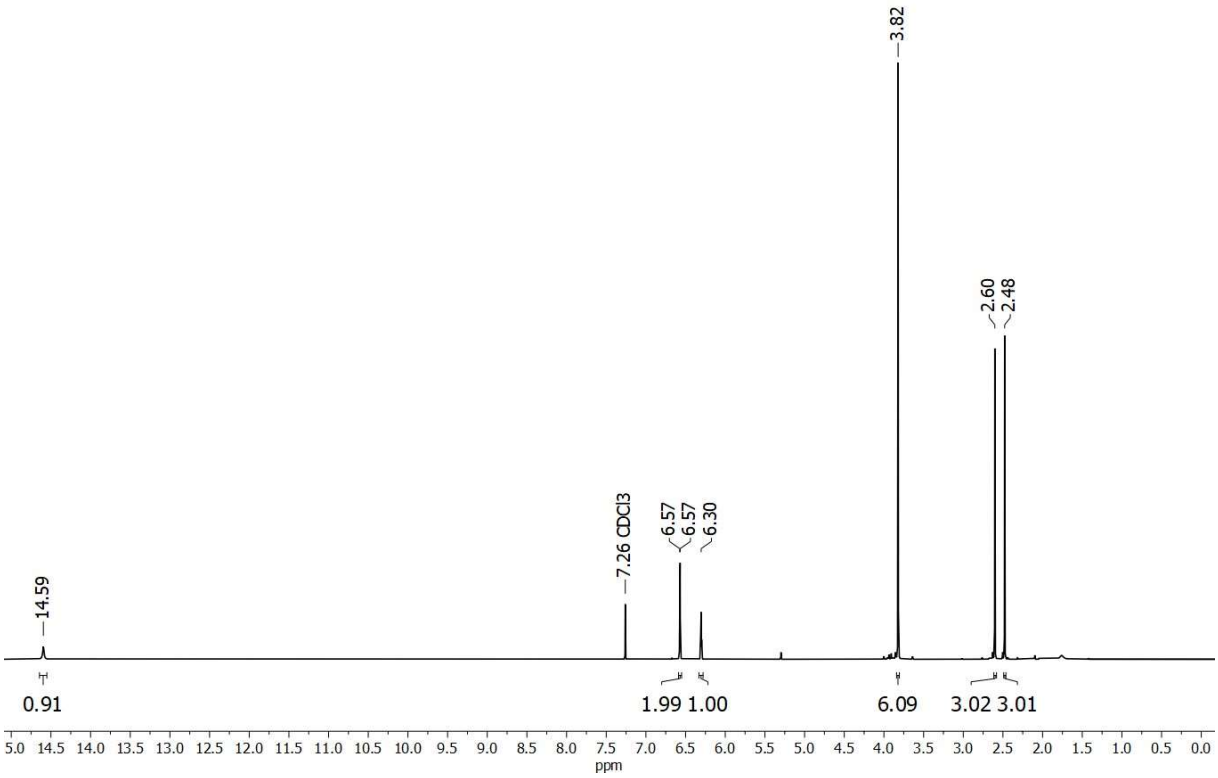


Figure S 36. ^{1}H-NMR spectra of compound **11b** dissolved in $CDCl_3$.

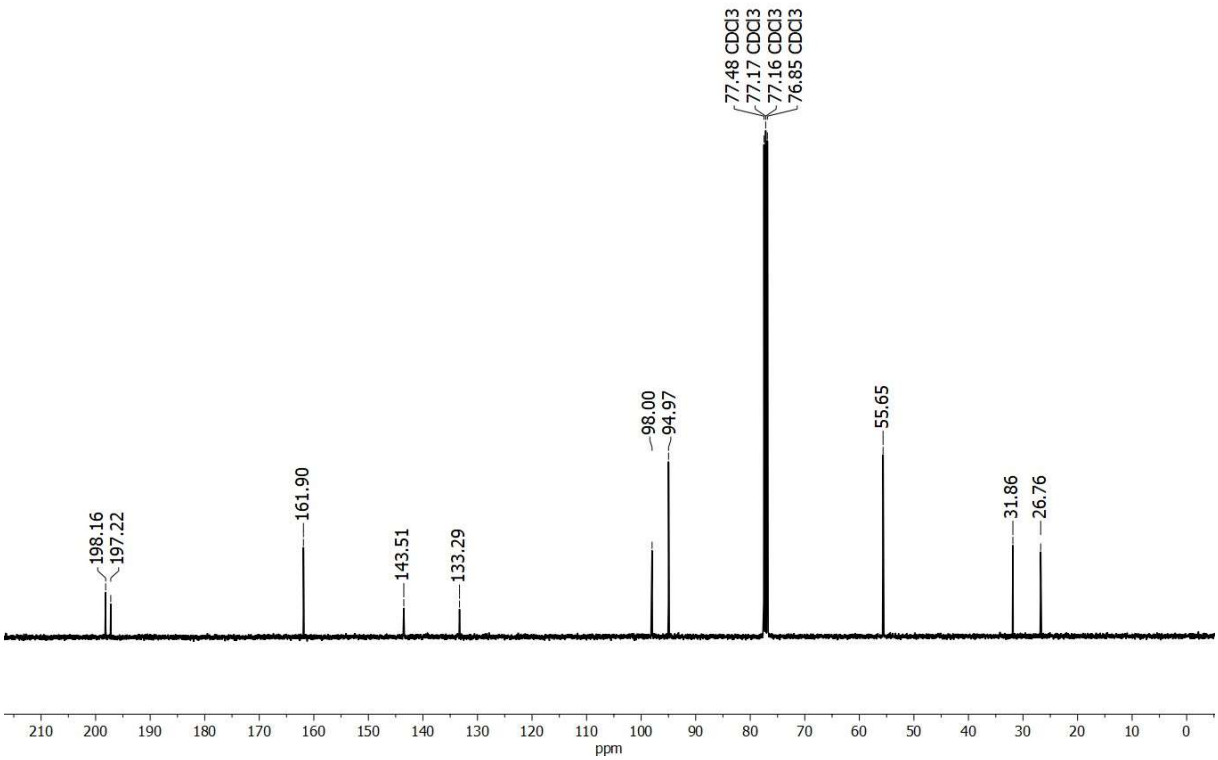


Figure S 37. ^{13}C-NMR spectra of compound **11b** dissolved in $CDCl_3$.

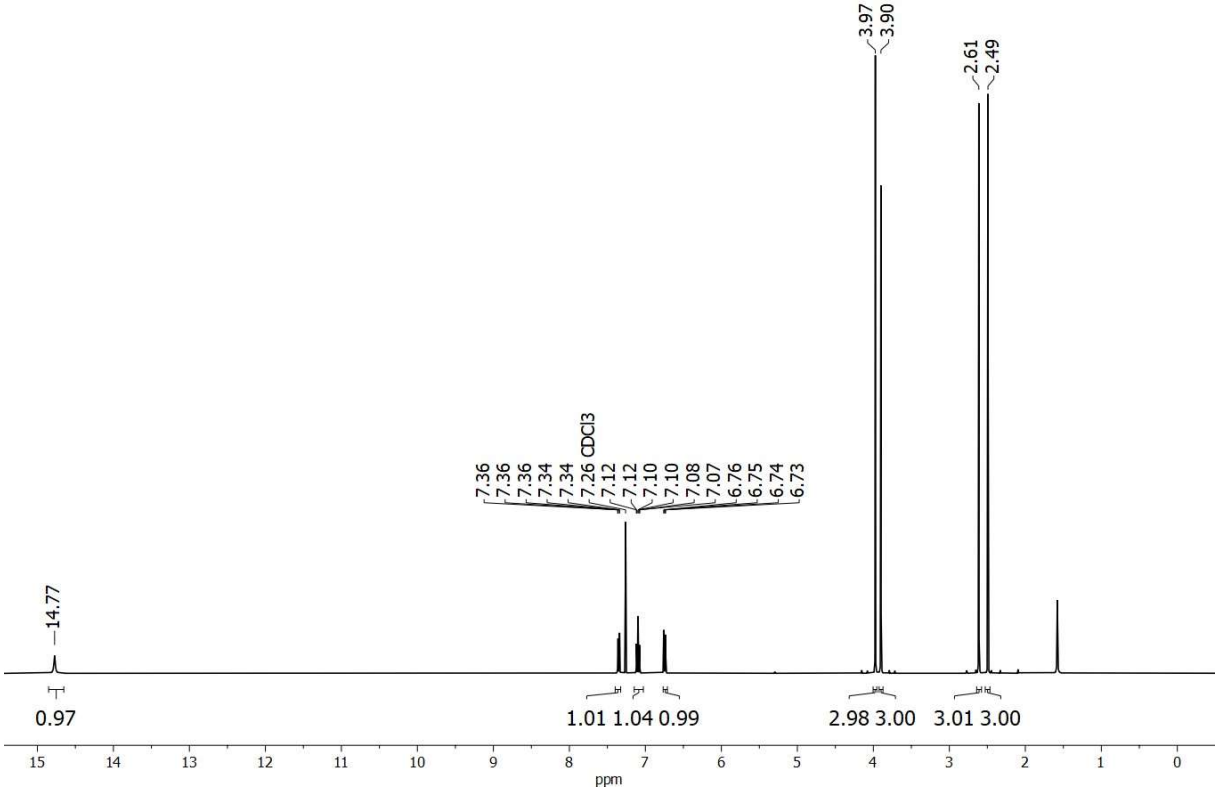


Figure S 38. ^{1}H-NMR spectra of compound **11c** dissolved in $CDCl_3$.

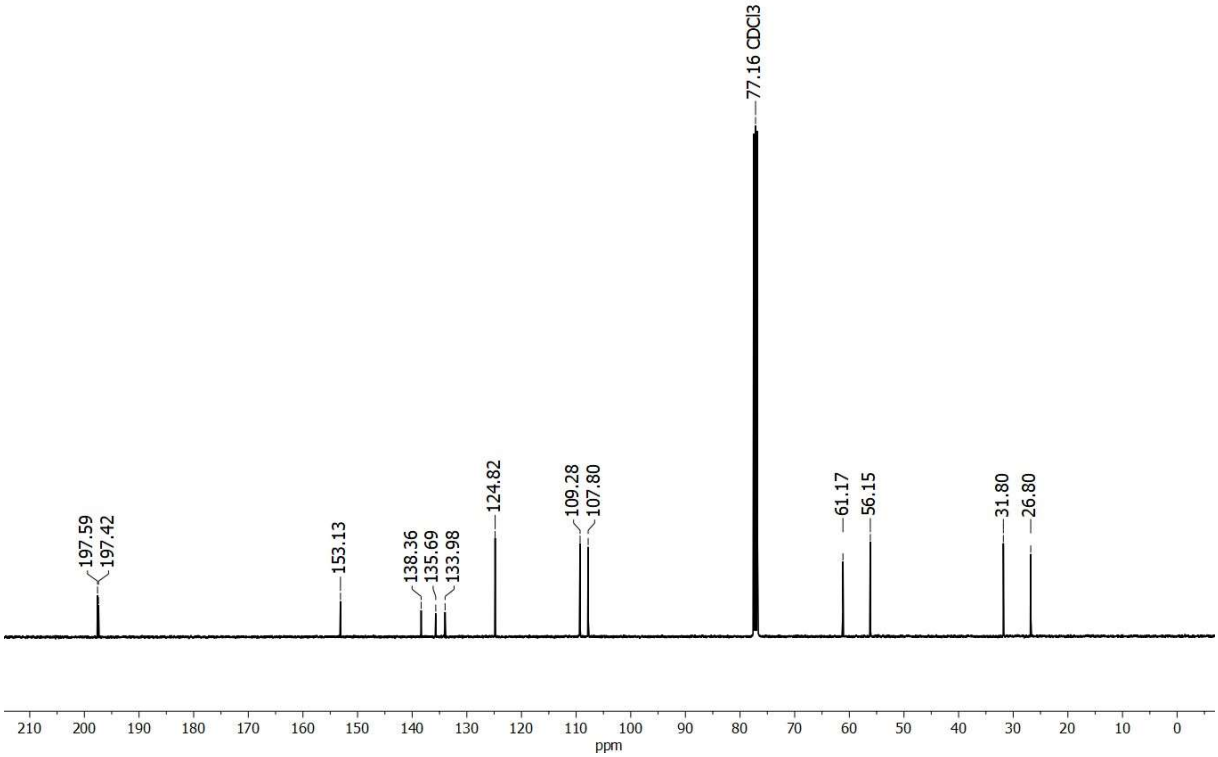


Figure S 39. ^{13}C-NMR spectra of compound **11c** dissolved in $CDCl_3$.

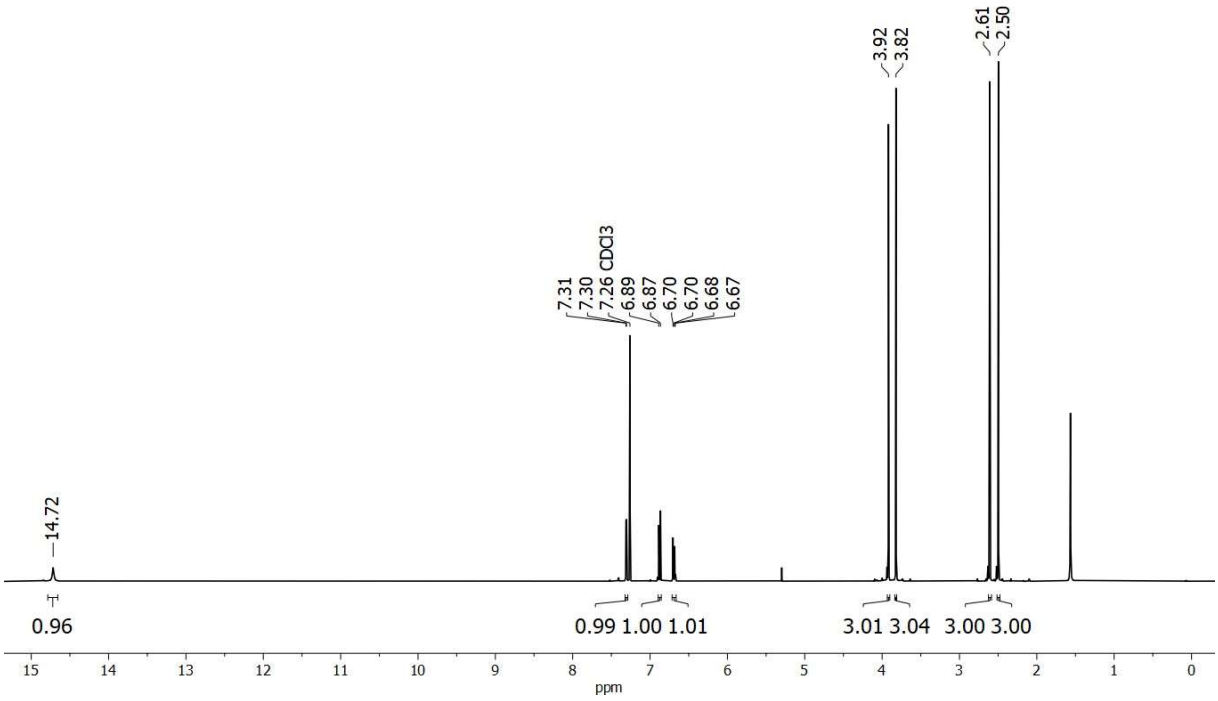


Figure S 40. ^{1}H-NMR spectra of compound **11d** dissolved in $CDCl_3$.

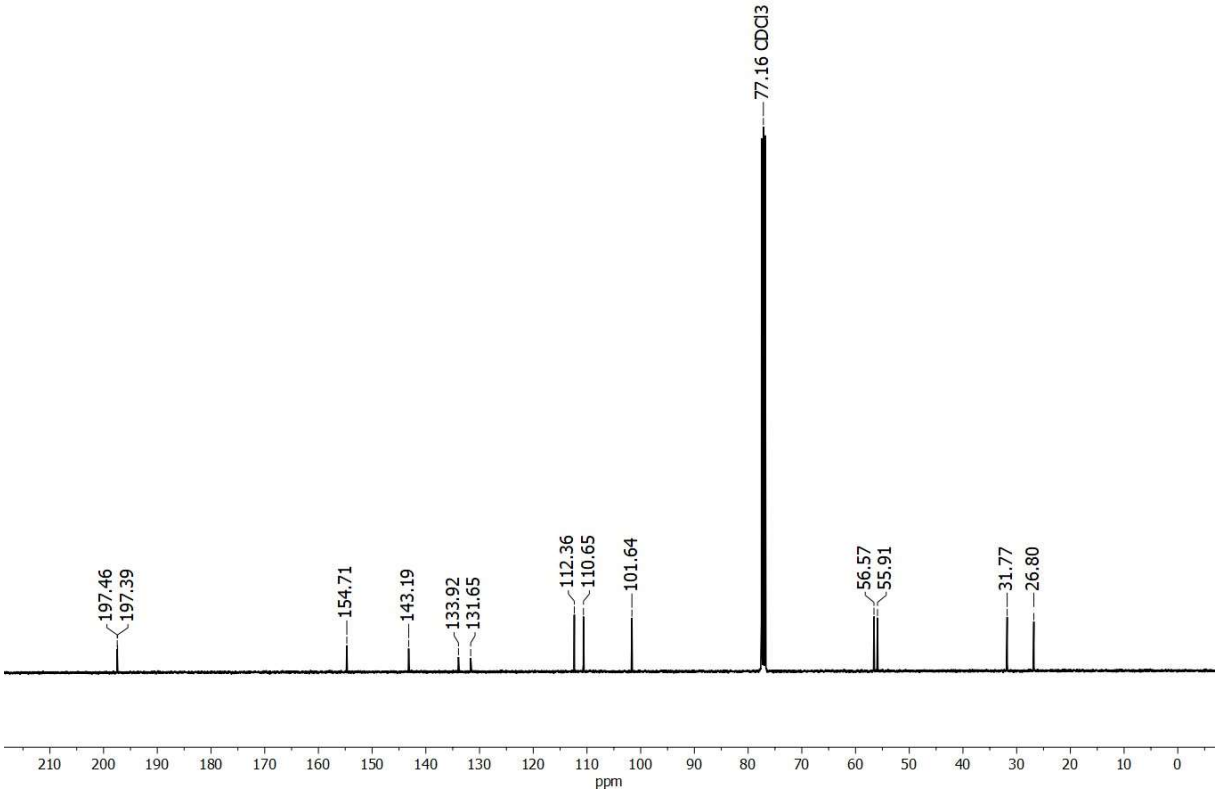


Figure S 41. ^{13}C-NMR spectra of compound **11d** dissolved in $CDCl_3$.

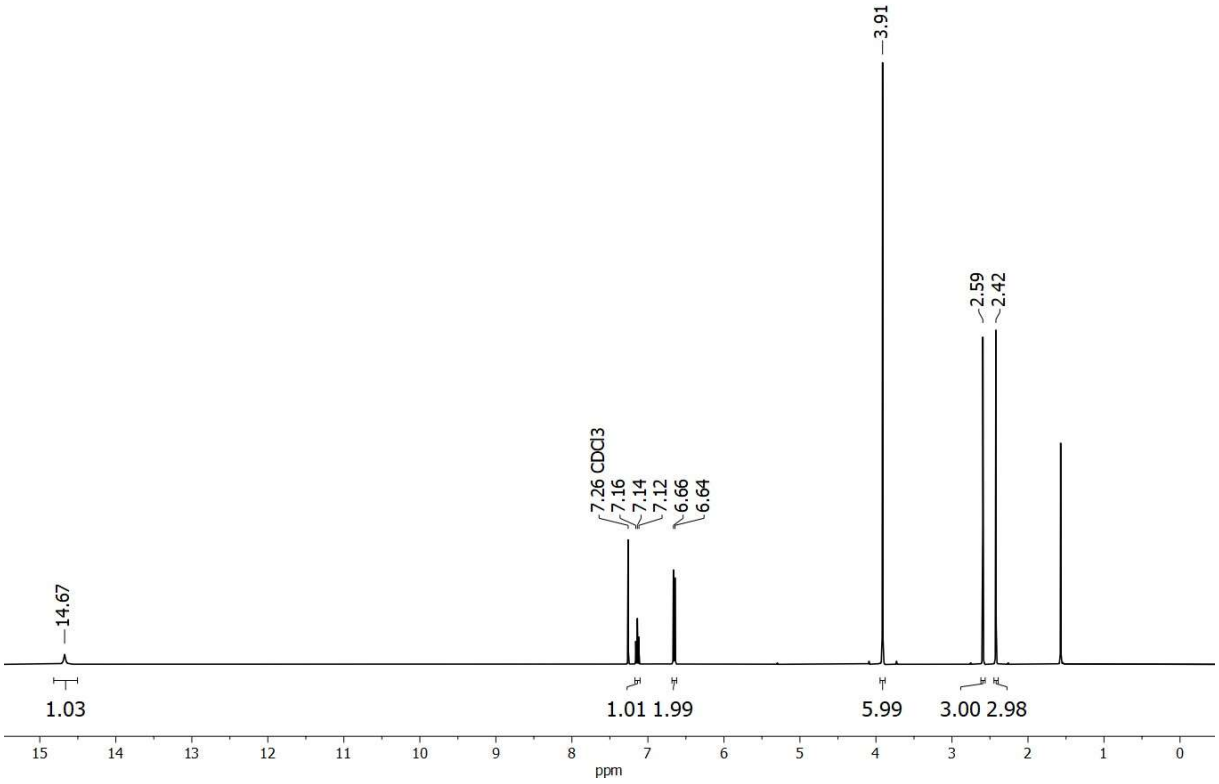


Figure S 42. ^{1}H-NMR spectra of compound **11e** dissolved in $CDCl_3$.

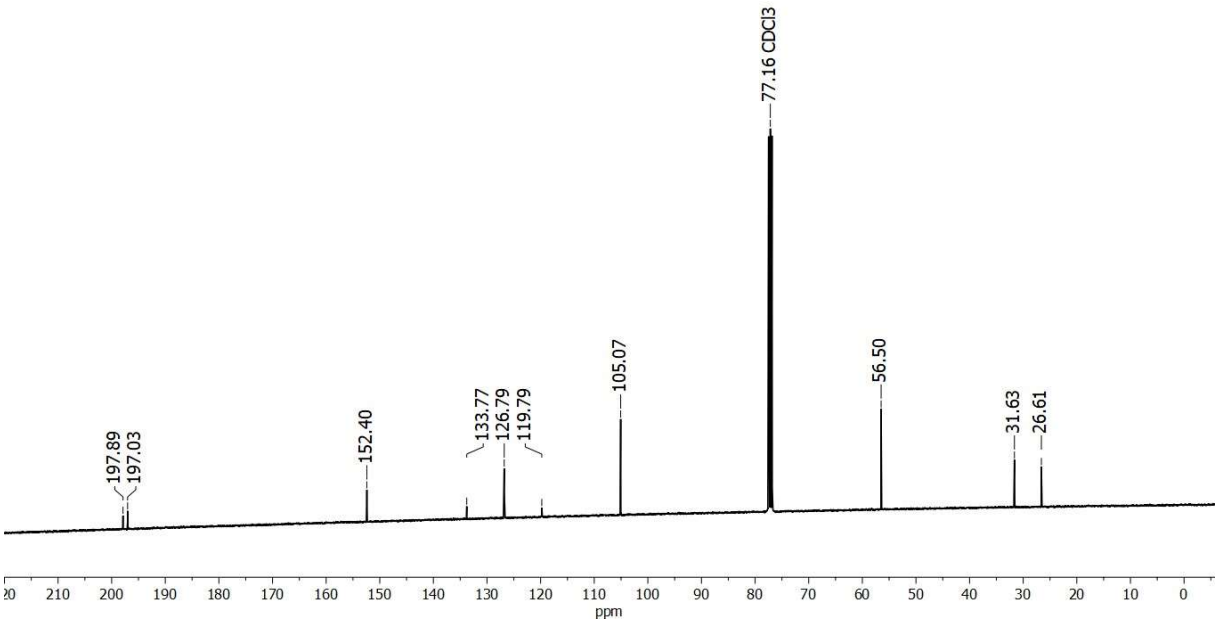


Figure S 43. ^{13}C-NMR spectra of compound **11e** dissolved in $CDCl_3$.

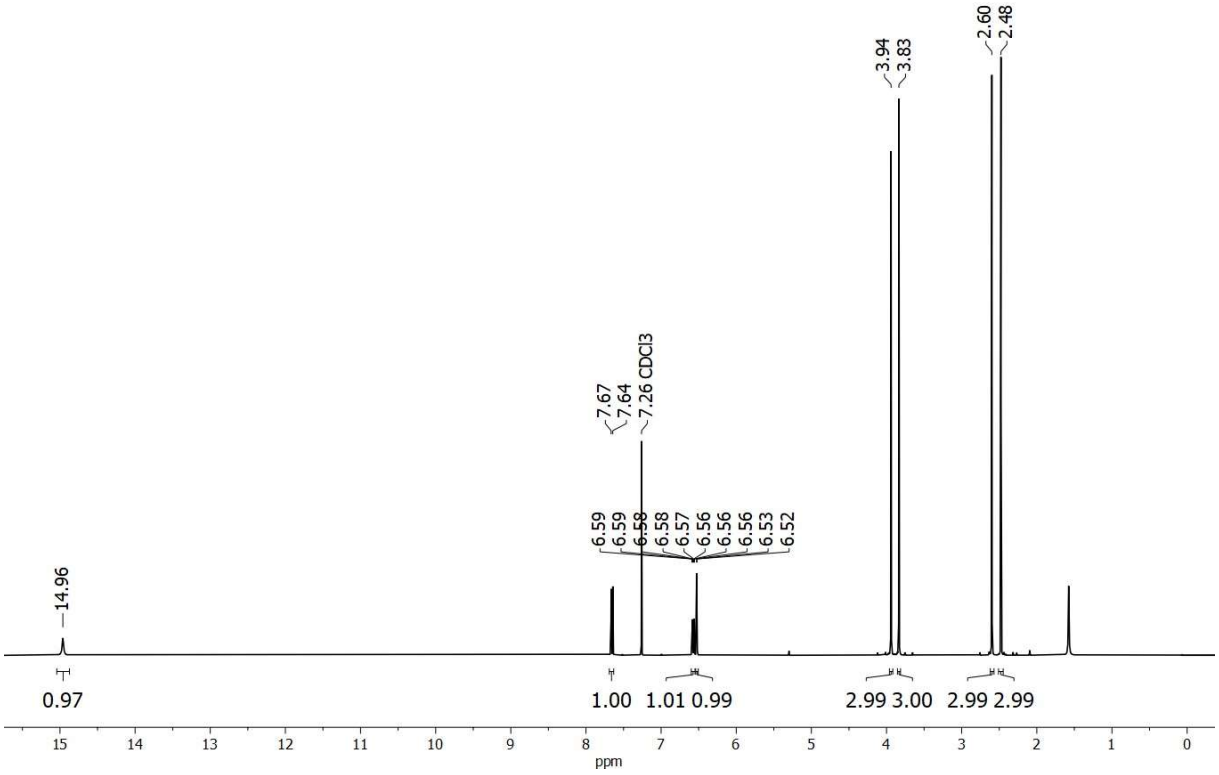


Figure S 44. ^{1}H-NMR spectra of compound **11f** dissolved in $CDCl_3$.

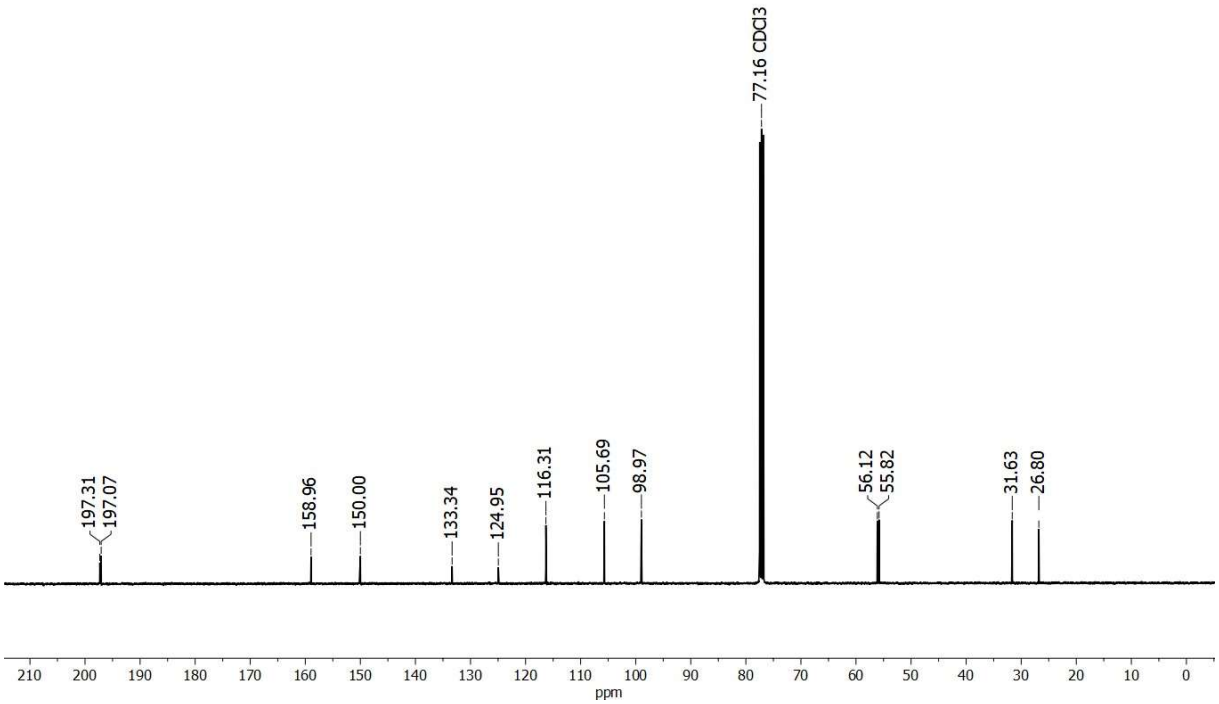


Figure S 45. ^{13}C-NMR spectra of compound **11f** dissolved in $CDCl_3$.

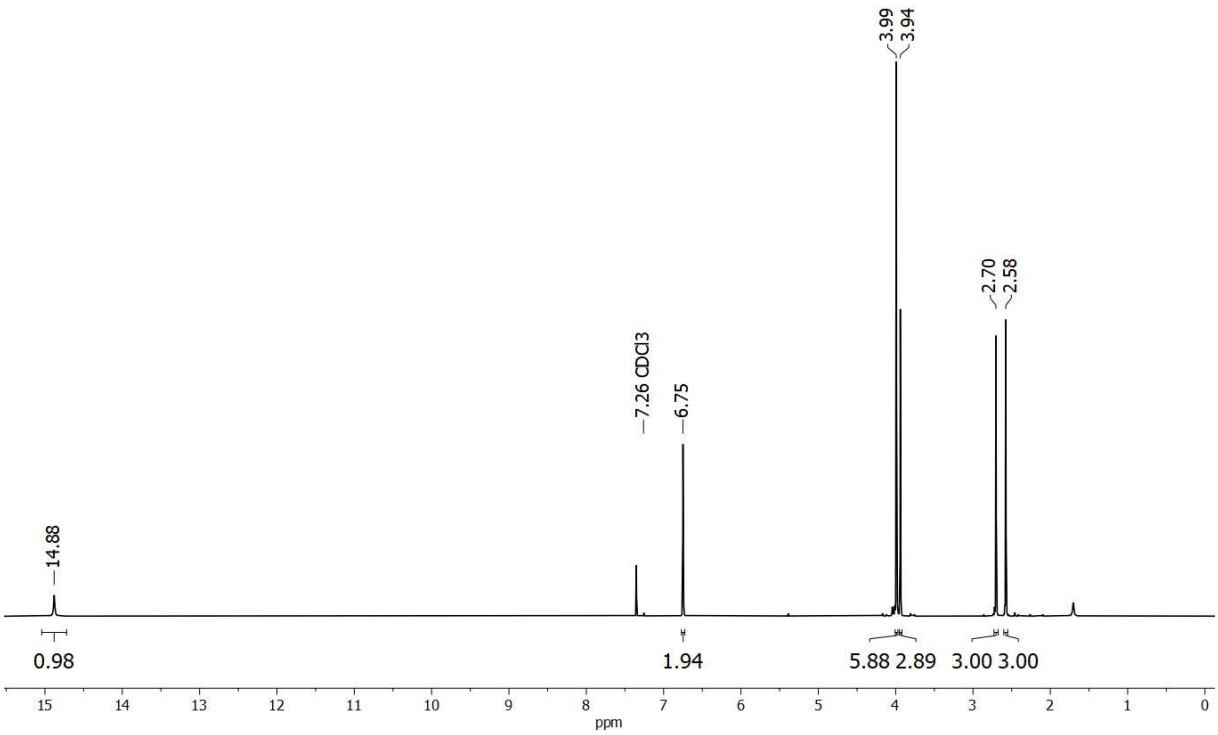


Figure S 46. ^{1}H-NMR spectra of compound **37a** dissolved in $CDCl_3$.

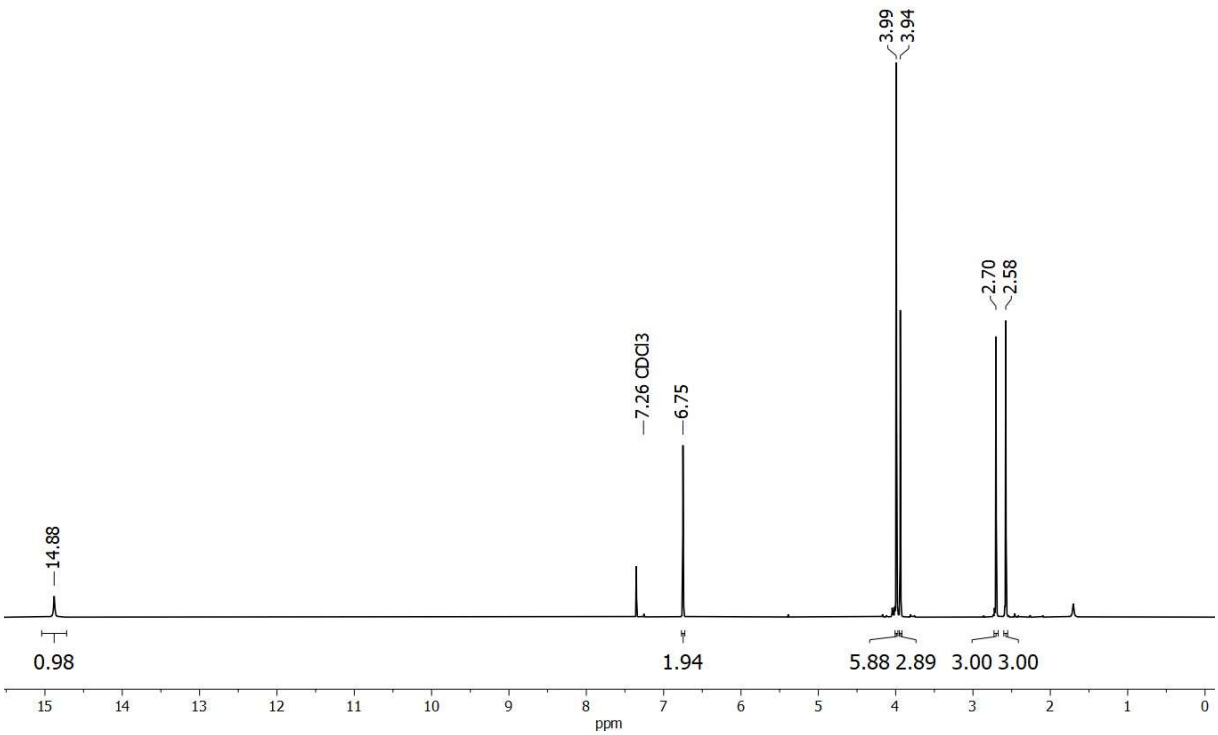


Figure S 47. ^{13}C-NMR spectra of compound **37a** dissolved in $CDCl_3$.

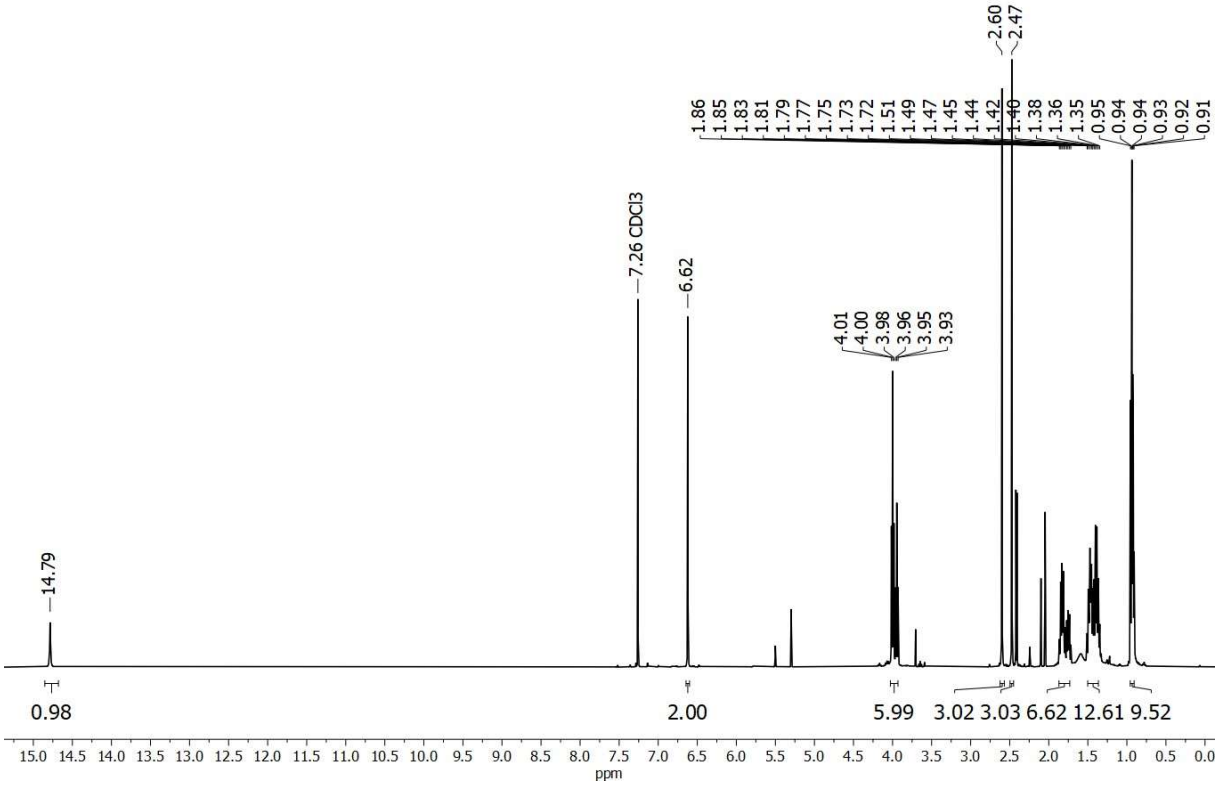


Figure S 48. ^{1}H-NMR spectra of compound **37b** dissolved in $CDCl_3$.

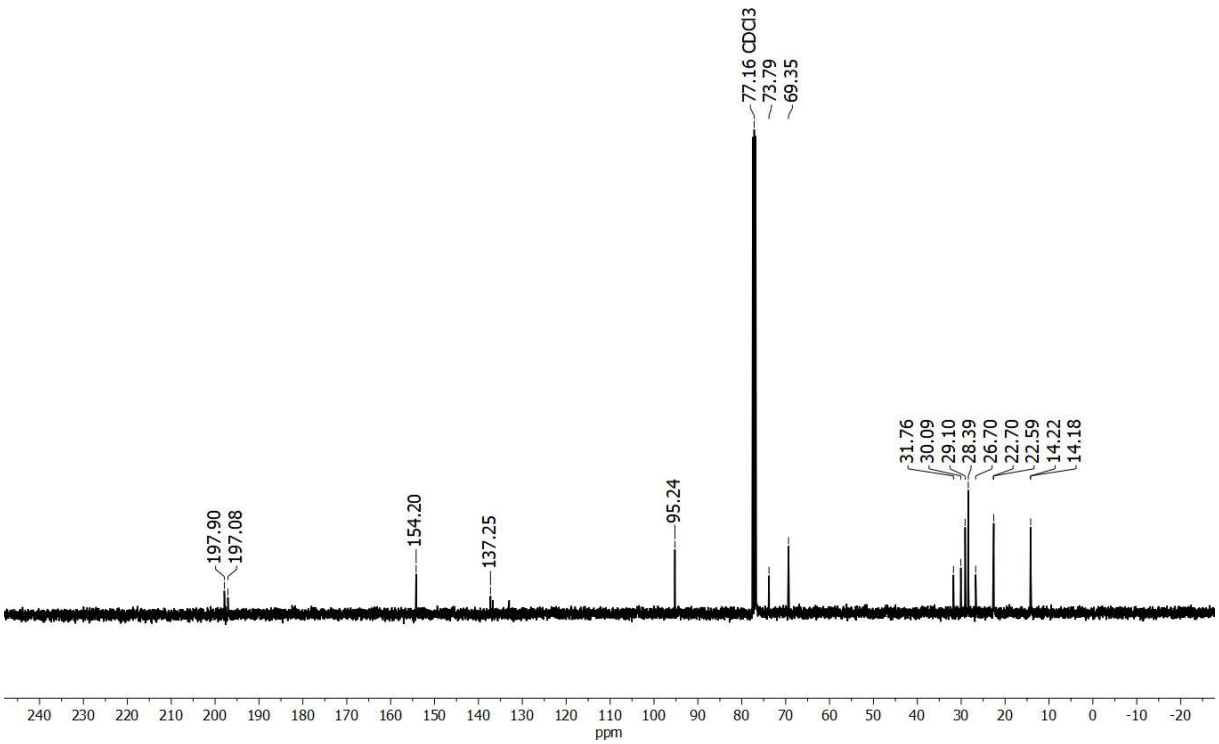


Figure S 49. ^{13}C-NMR spectra of compound **37b** dissolved in $CDCl_3$.

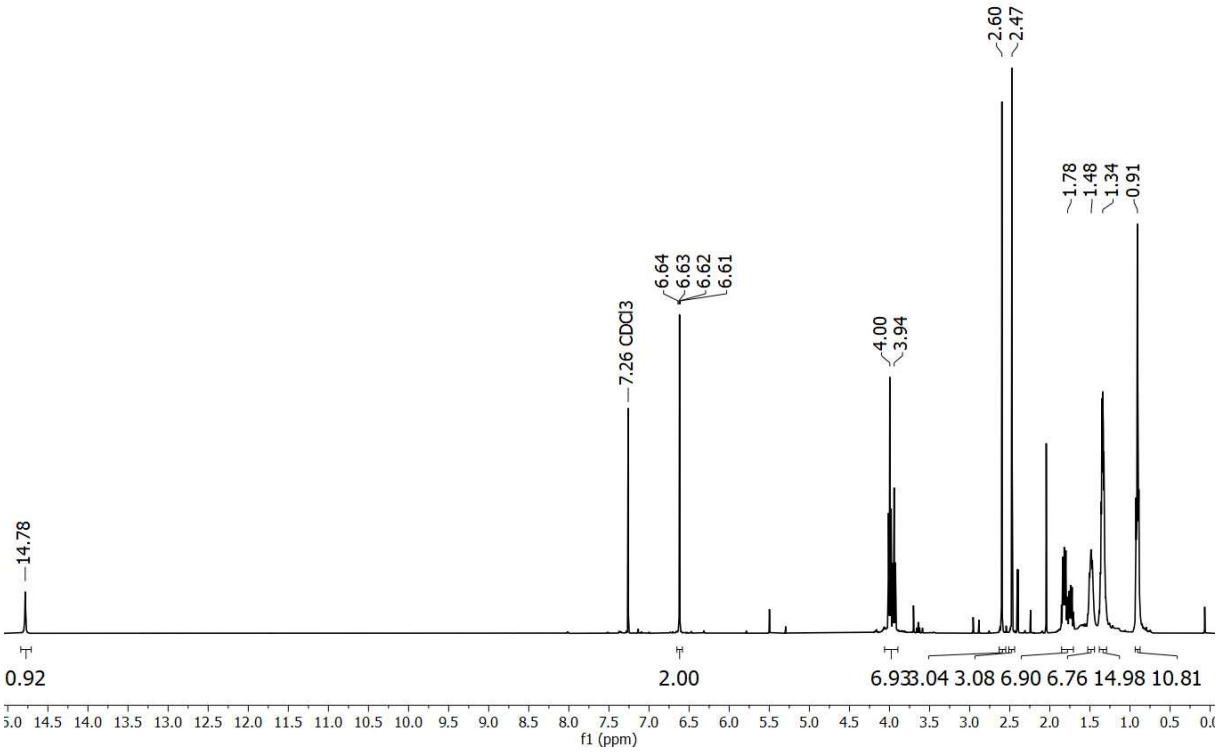


Figure S50. ^{1}H-NMR spectra of compound **37c** dissolved in $CDCl_3$.

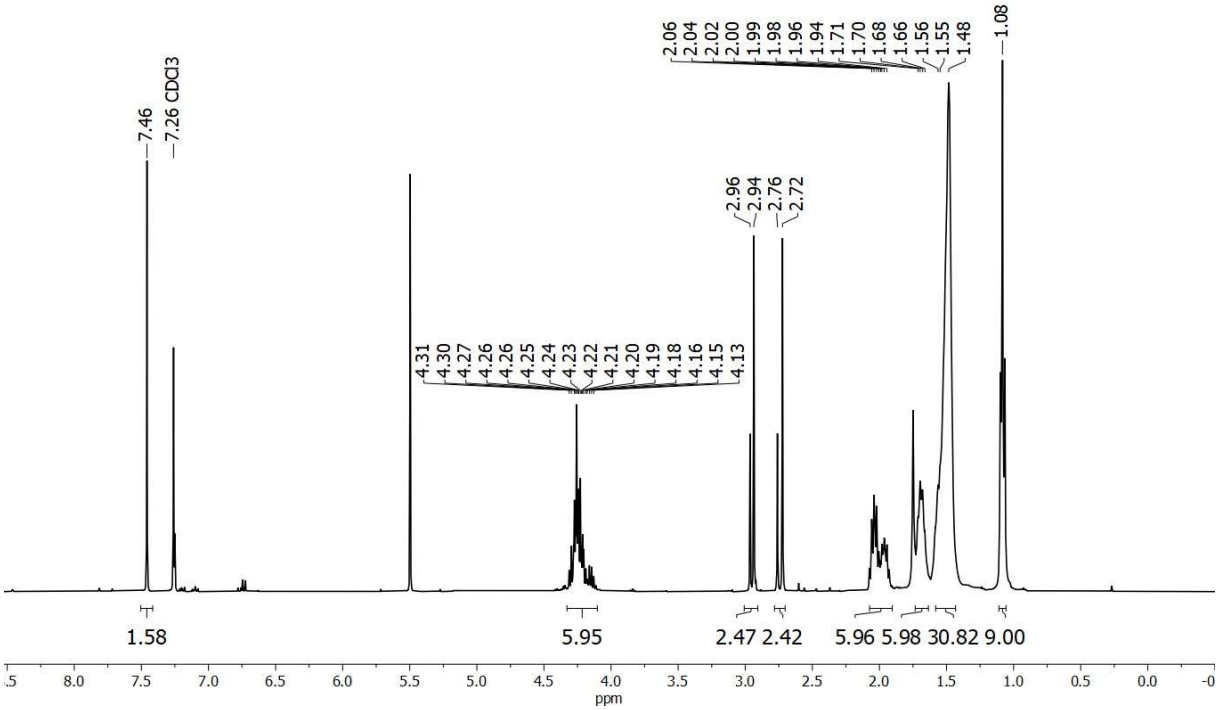


Figure S51. ^{1}H-NMR spectra of compound **37d** dissolved in $CDCl_3$.

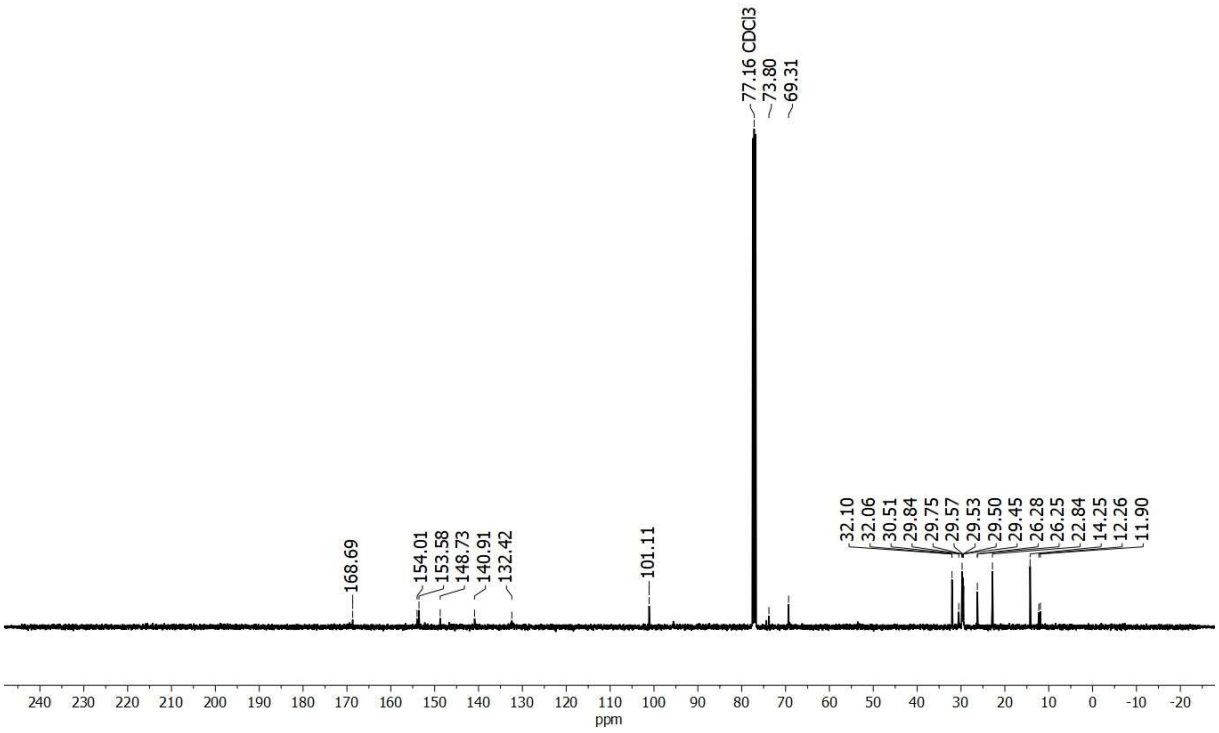


Figure S52. ^{13}C-NMR spectra of compound **37d** dissolved in $CDCl_3$.

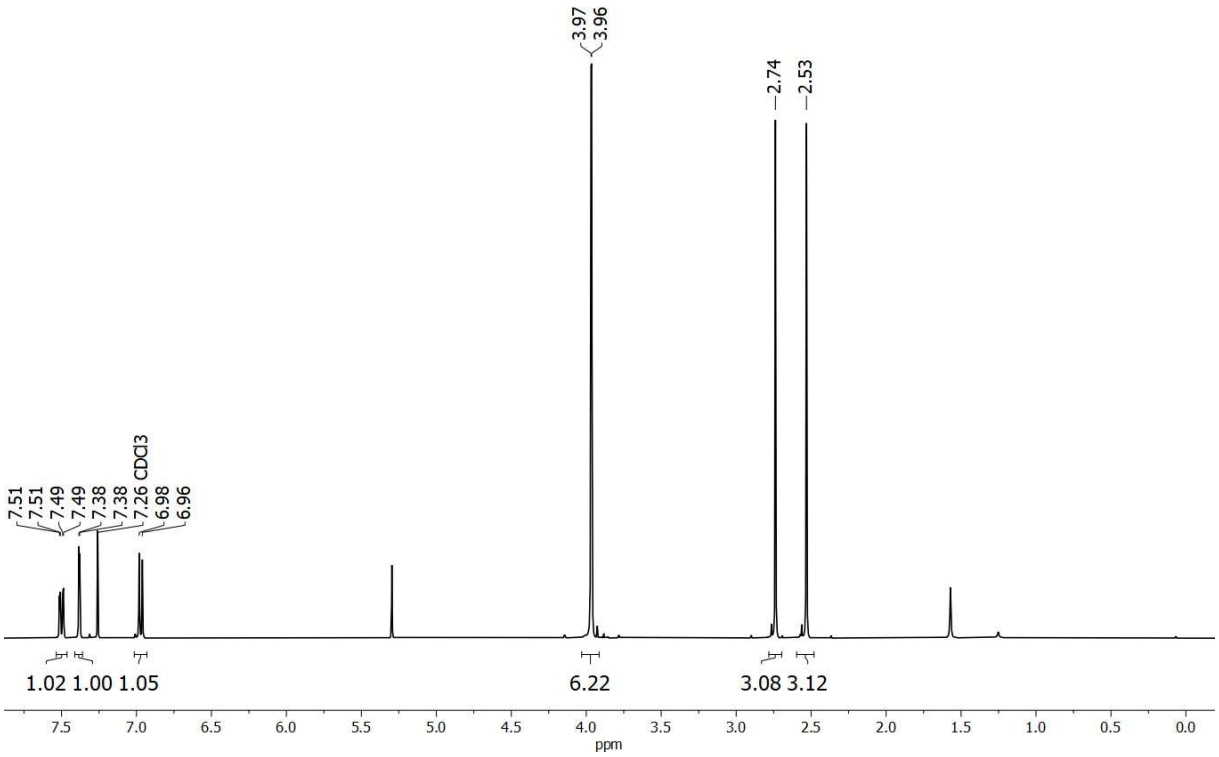


Figure S53. ^{1}H-NMR spectra of compound **1a** dissolved in $CDCl_3$.

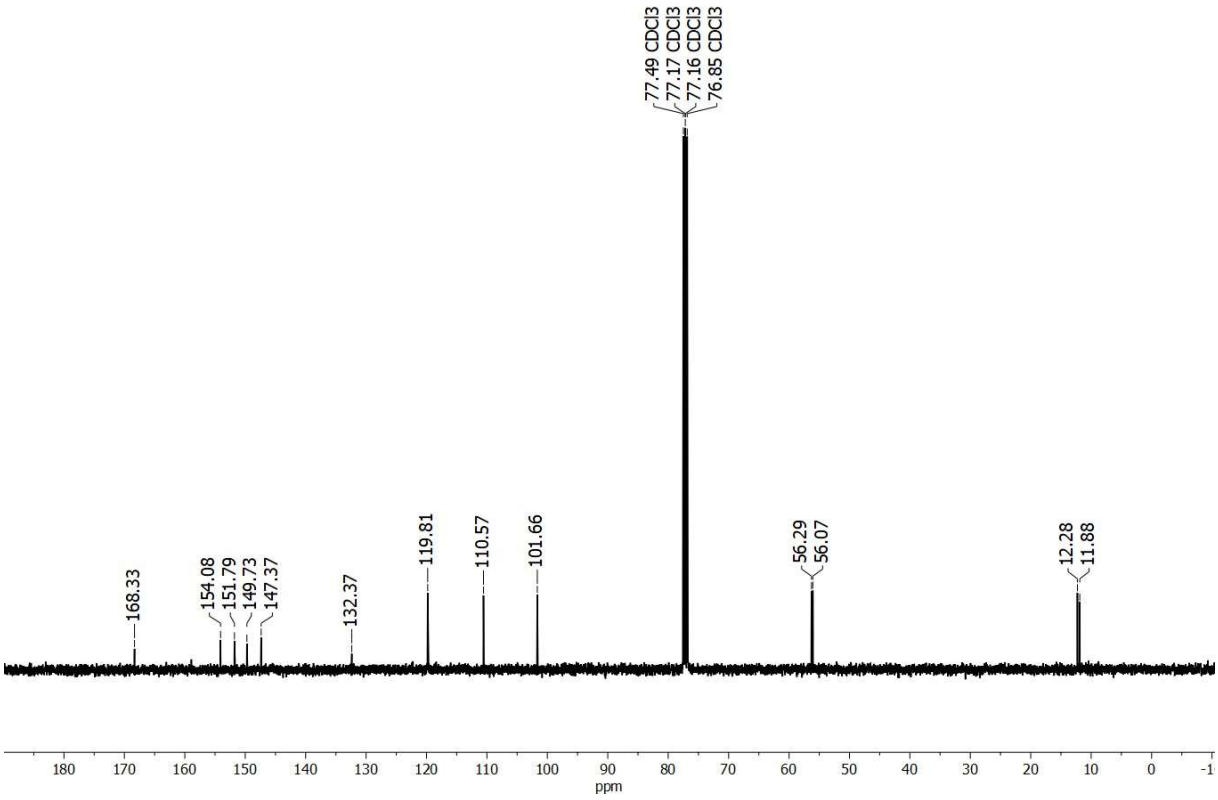


Figure S54. ^{13}C-NMR spectra of compound **1a** dissolved in $CDCl_3$.

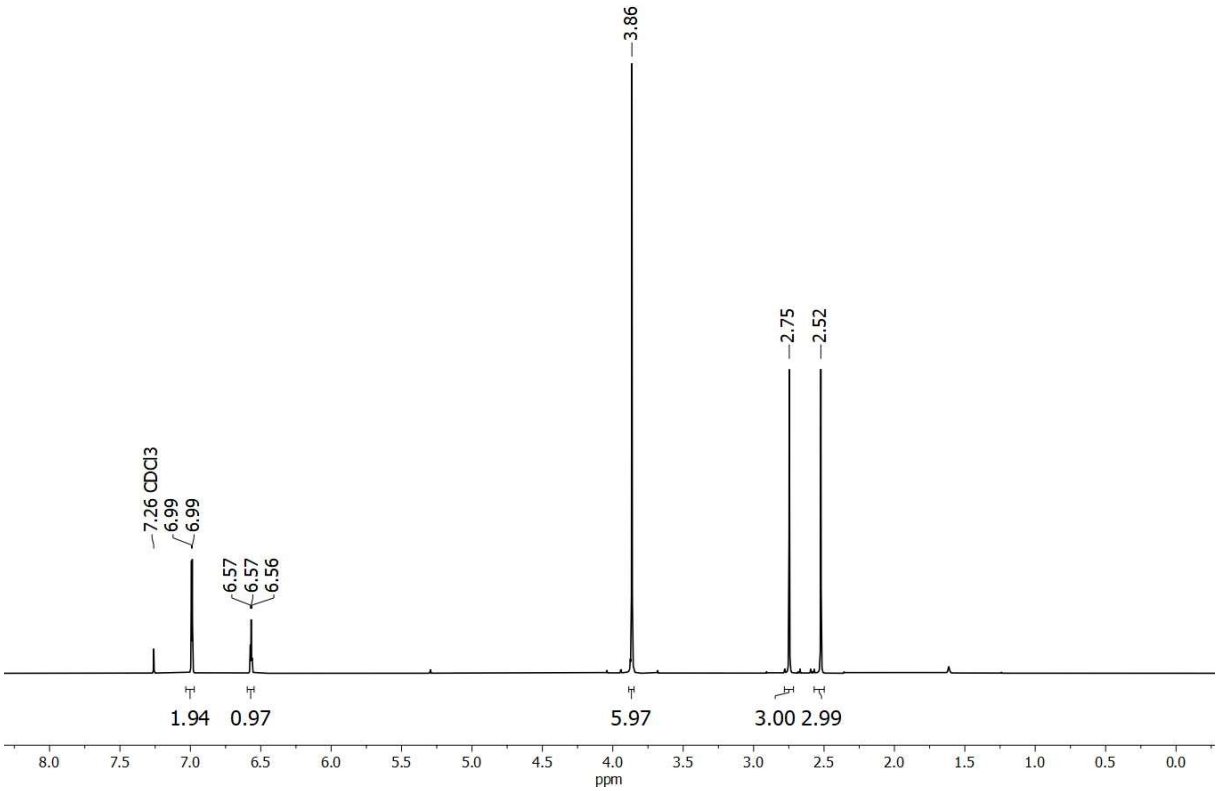


Figure S55. ^{1}H-NMR spectra of compound **1b** dissolved in $CDCl_3$.

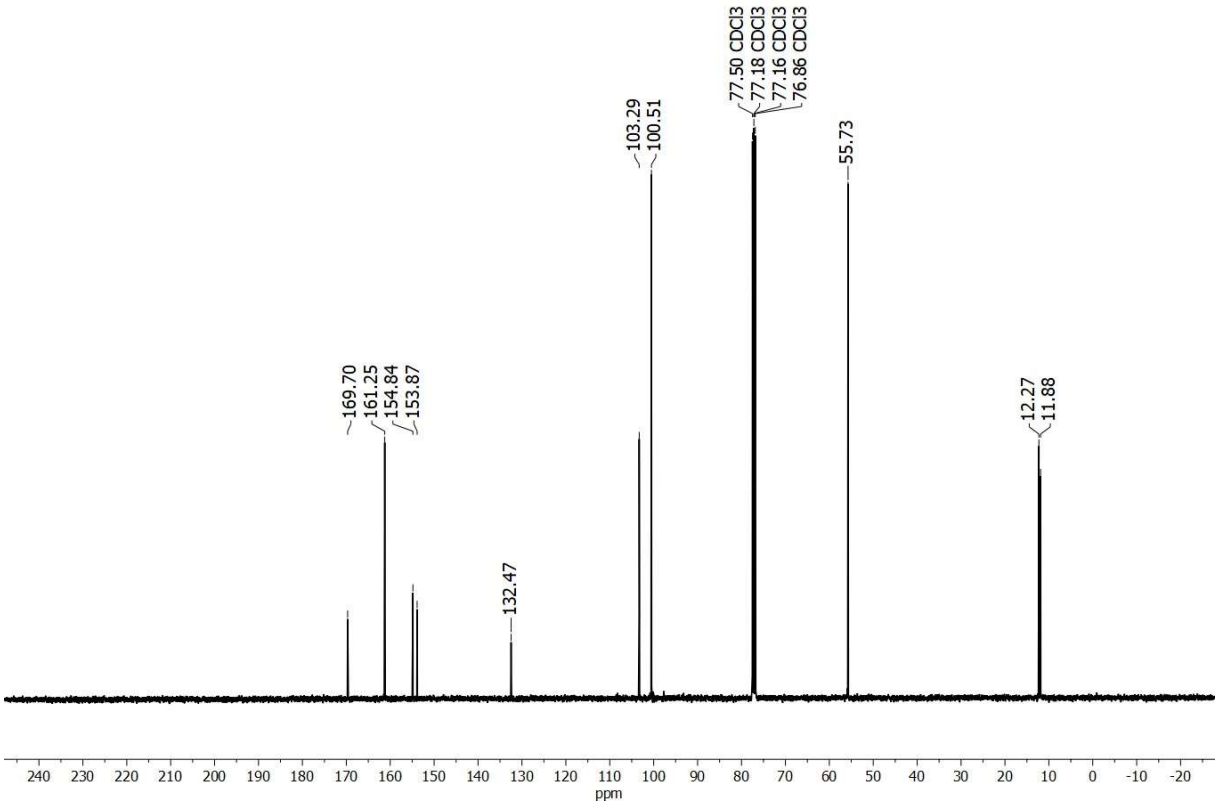


Figure S56. ^{13}C-NMR spectra of compound **1b** dissolved in $CDCl_3$.

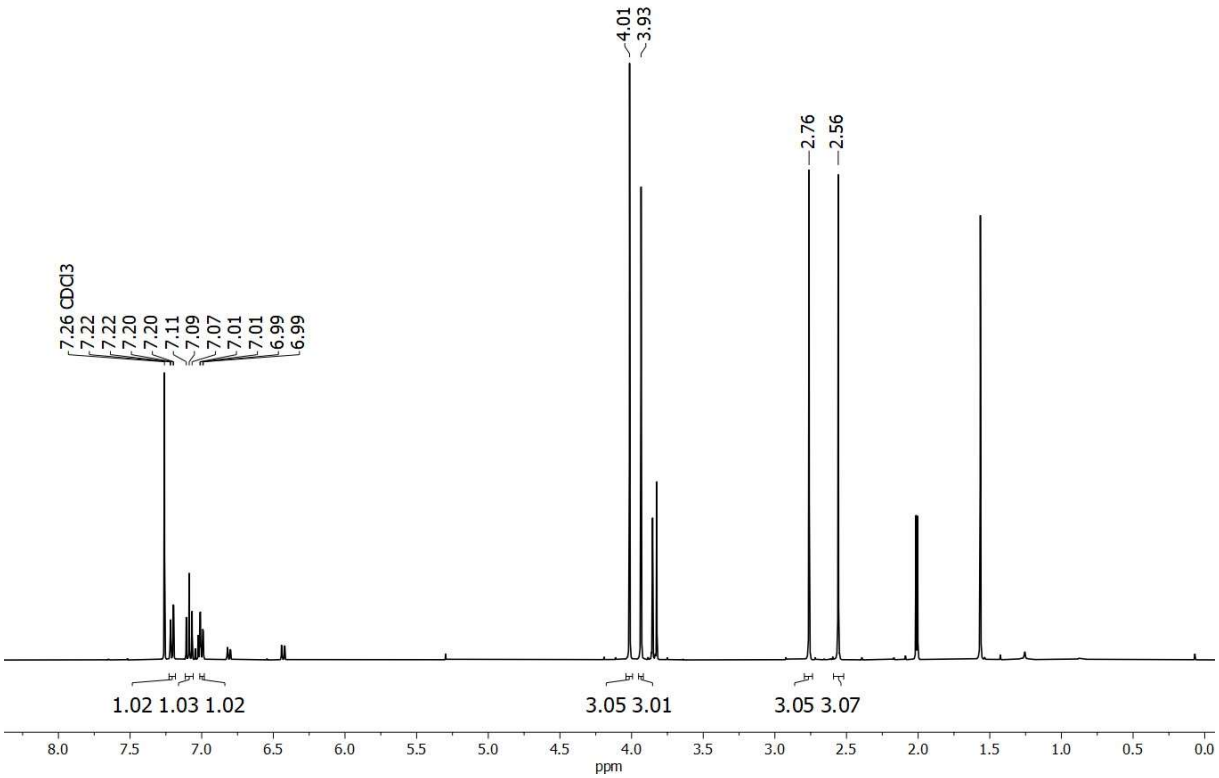


Figure S57. ^{1}H-NMR spectra of compound **1c** dissolved in $CDCl_3$.

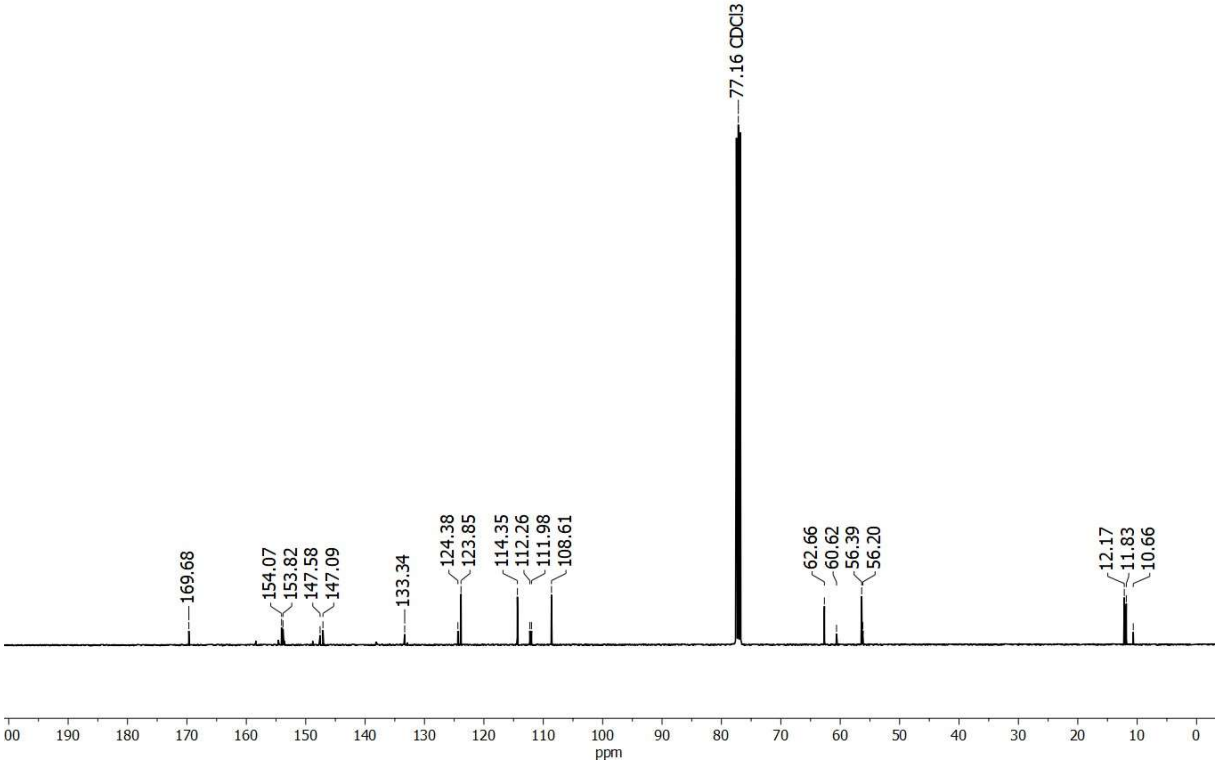


Figure S58. ^{1}H-NMR spectra of compound **1c** dissolved in $CDCl_3$.

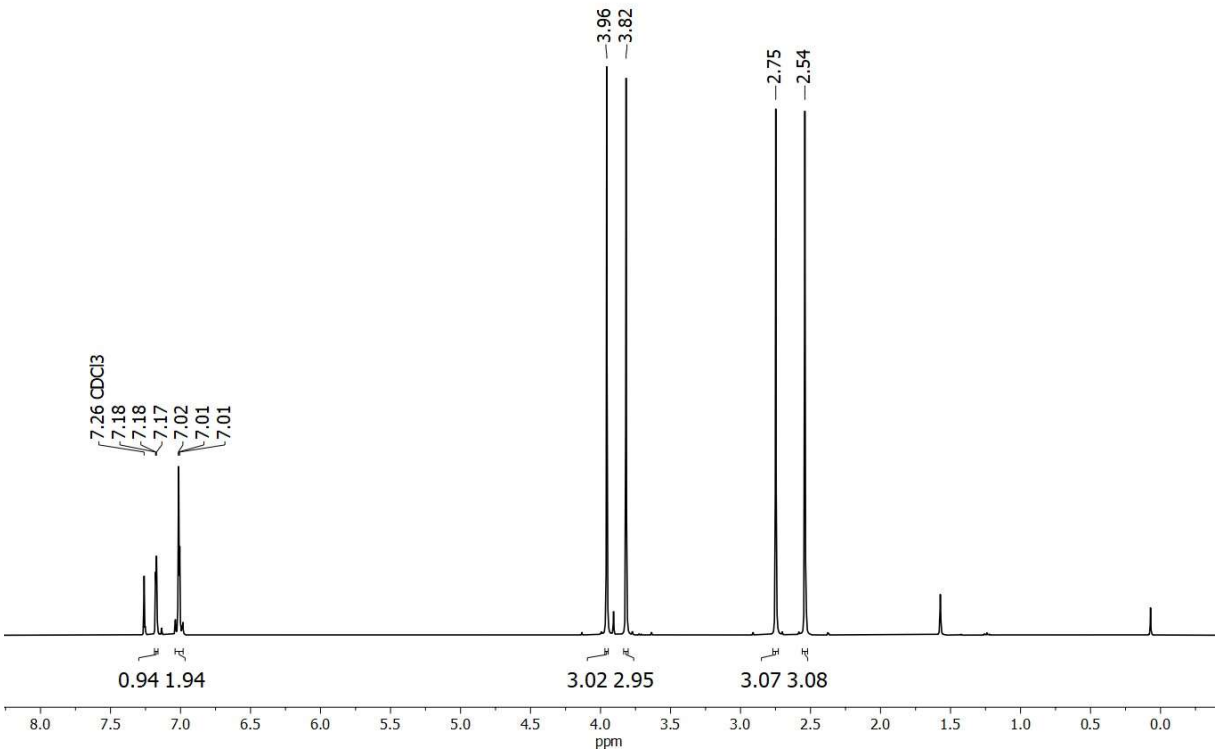


Figure S59. ^{1}H-NMR spectra of compound **1d** dissolved in $CDCl_3$.

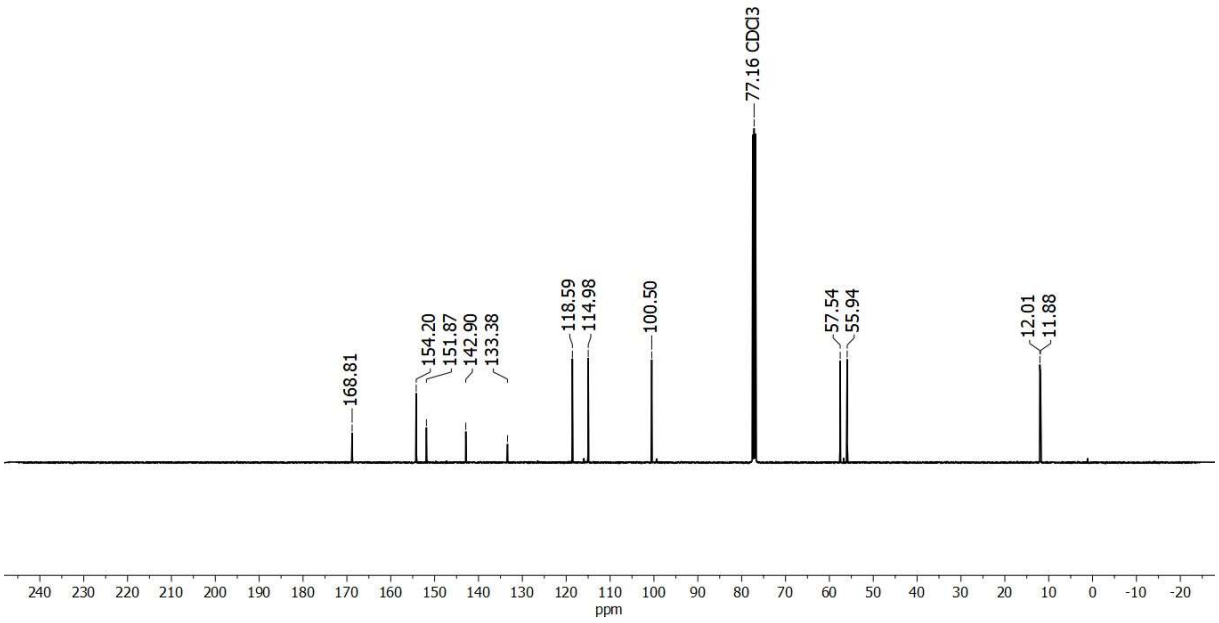


Figure S60. ^{13}C-NMR spectra of compound **1d** dissolved in $CDCl_3$.

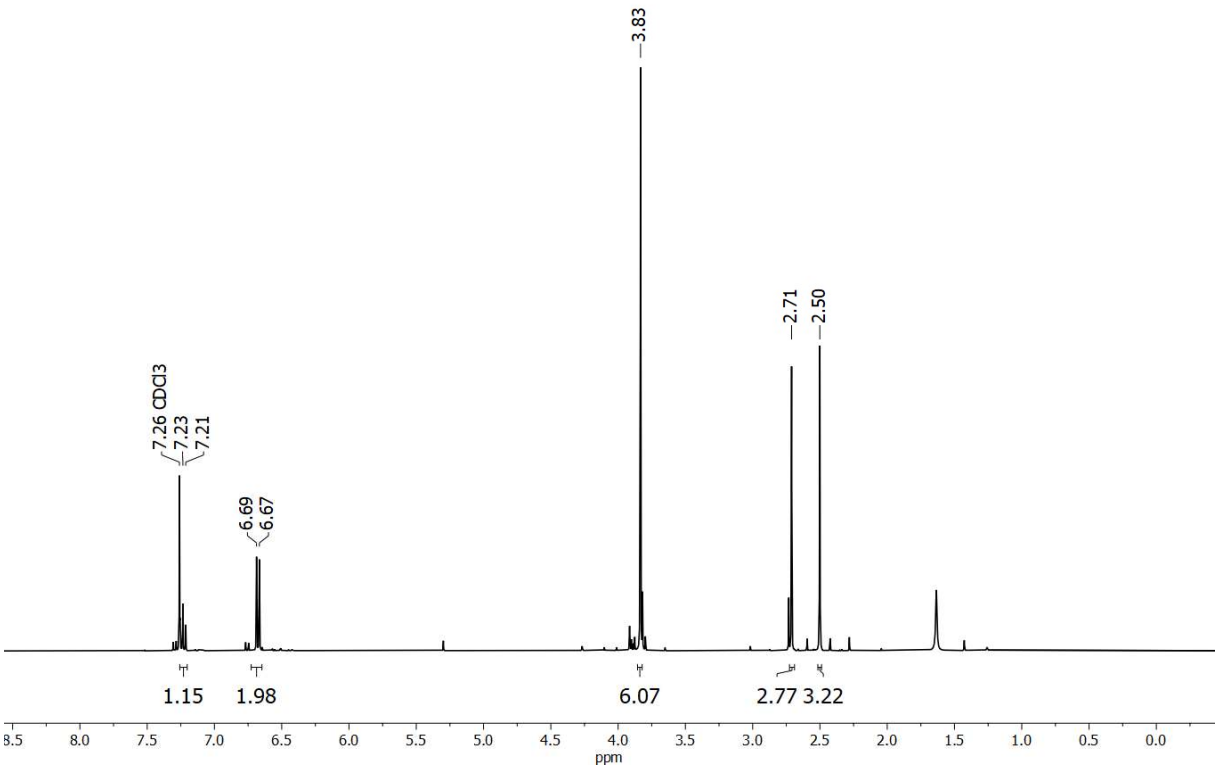


Figure S61. ^{1}H-NMR spectra of compound **1e** dissolved in $CDCl_3$.

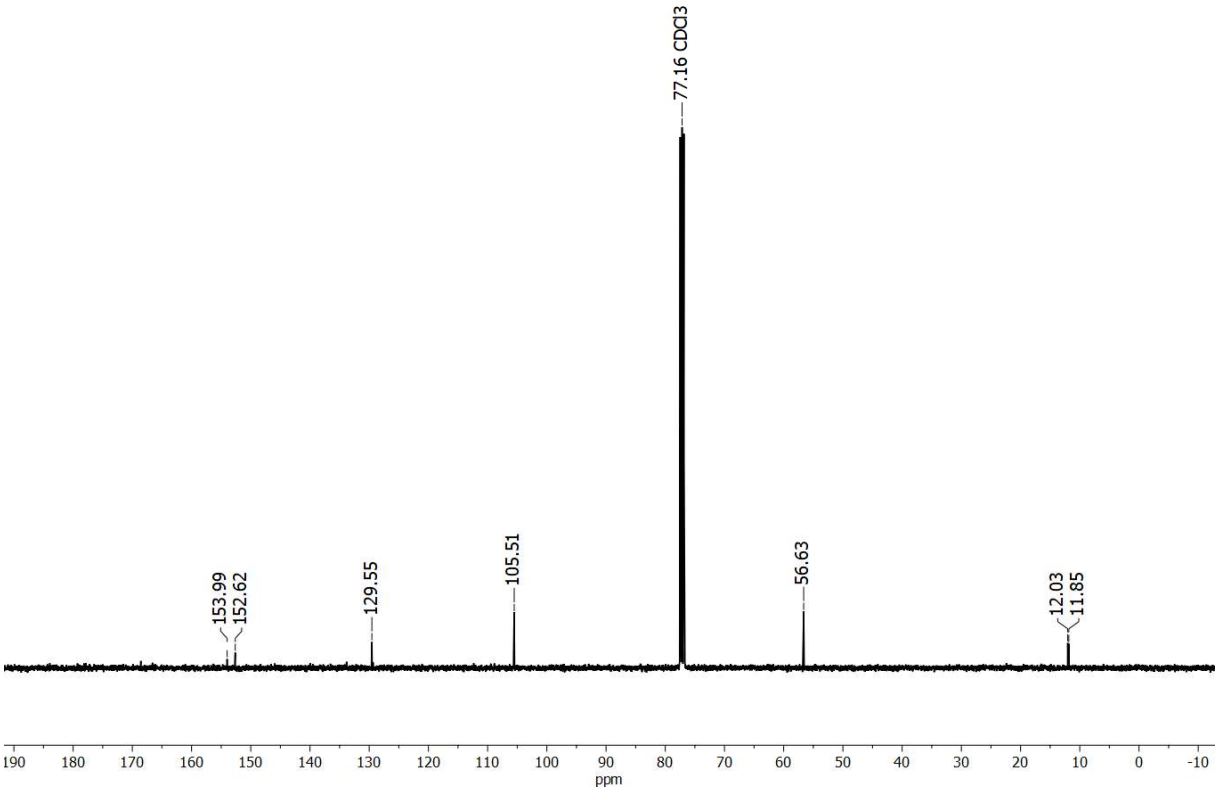


Figure S62. ^{13}C-NMR spectra of compound **1e** dissolved in $CDCl_3$.

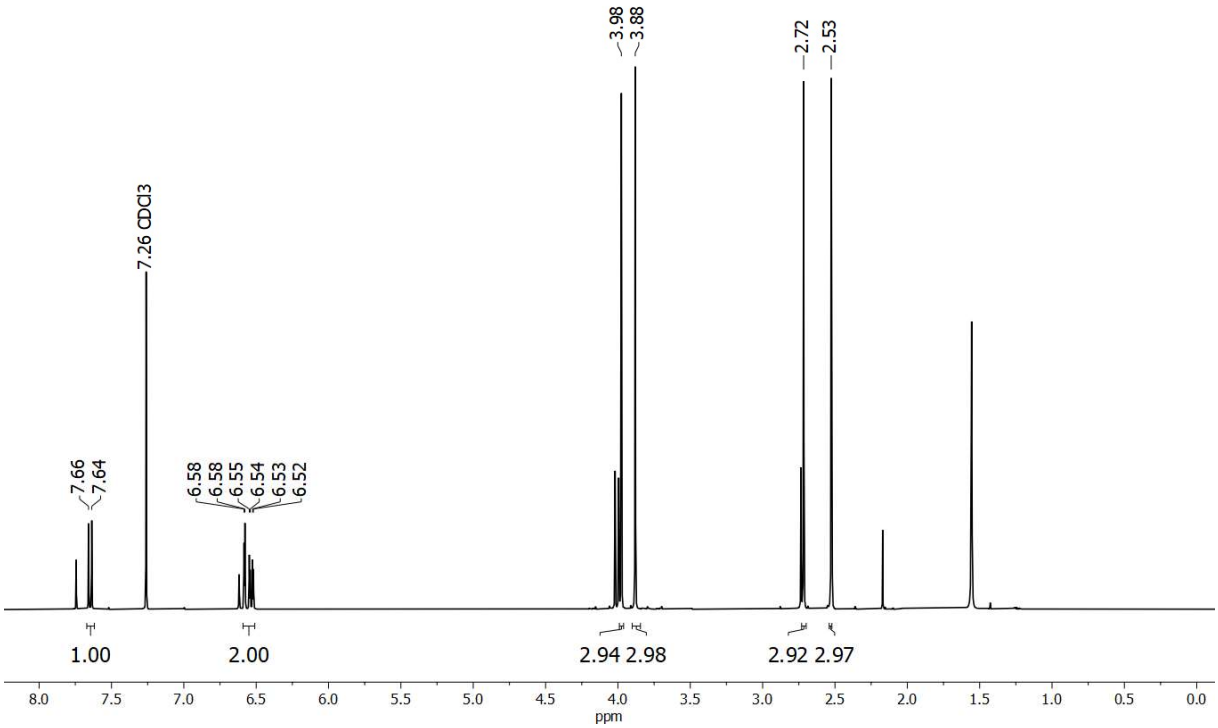


Figure S63. ^{1}H-NMR spectra of compound **1f** dissolved in $CDCl_3$.

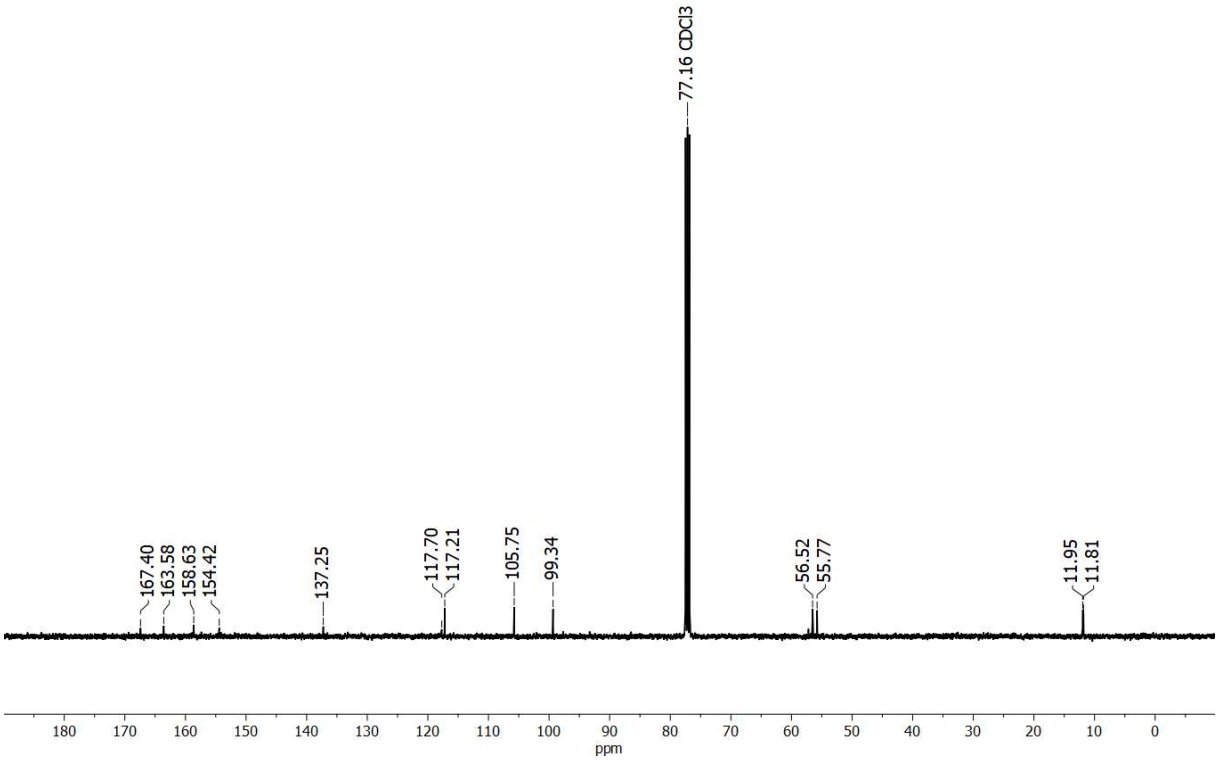


Figure S64. ^{13}C-NMR spectra of compound **1f** dissolved in $CDCl_3$.

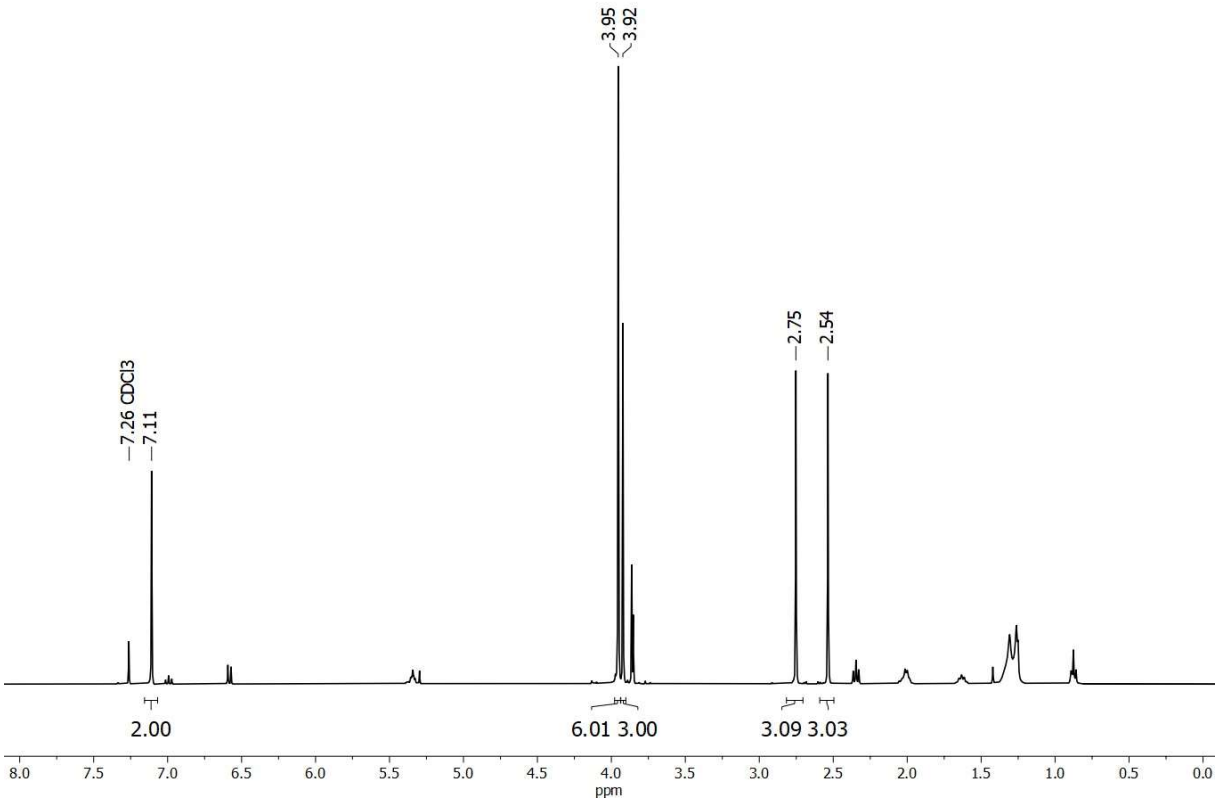


Figure S65. ^{1}H-NMR spectra of compound **3a** dissolved in $CDCl_3$.

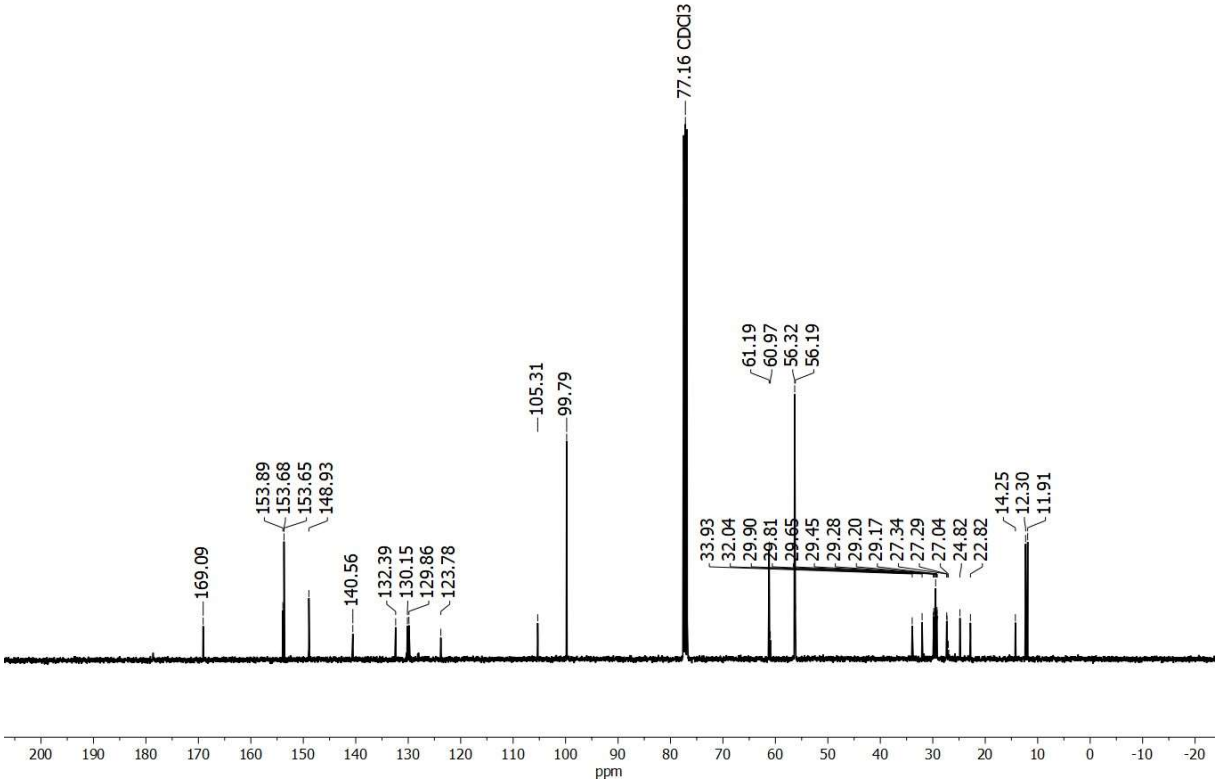


Figure S66. ^{13}C-NMR spectra of compound **3a** dissolved in $CDCl_3$.

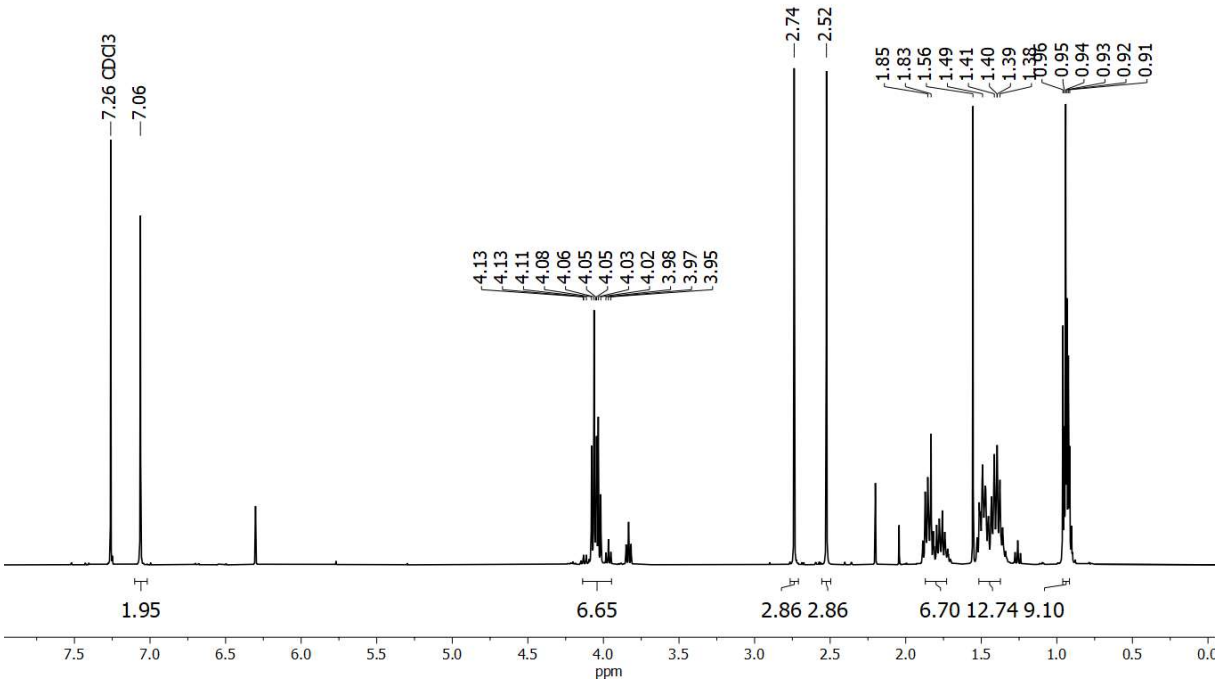


Figure S67. ^{1}H-NMR spectra of compound **3b** dissolved in $CDCl_3$.

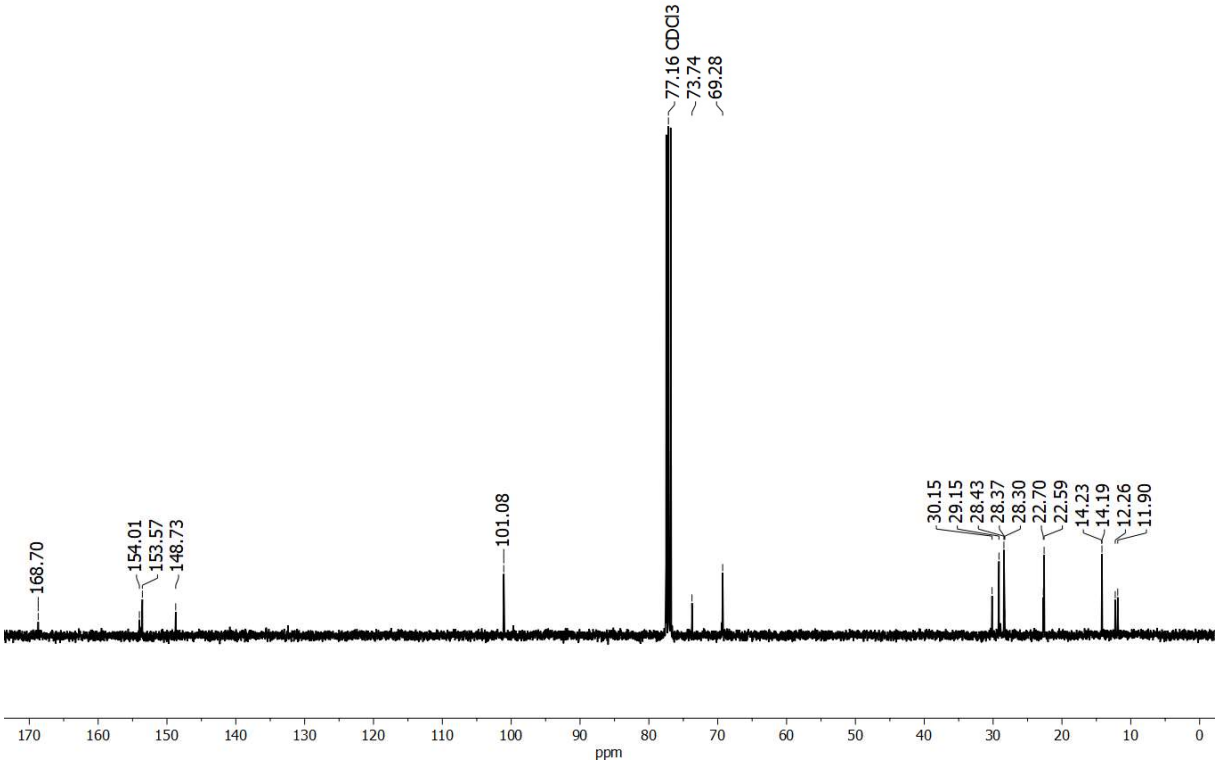


Figure S68. ^{13}C-NMR spectra of compound **3b** dissolved in $CDCl_3$.

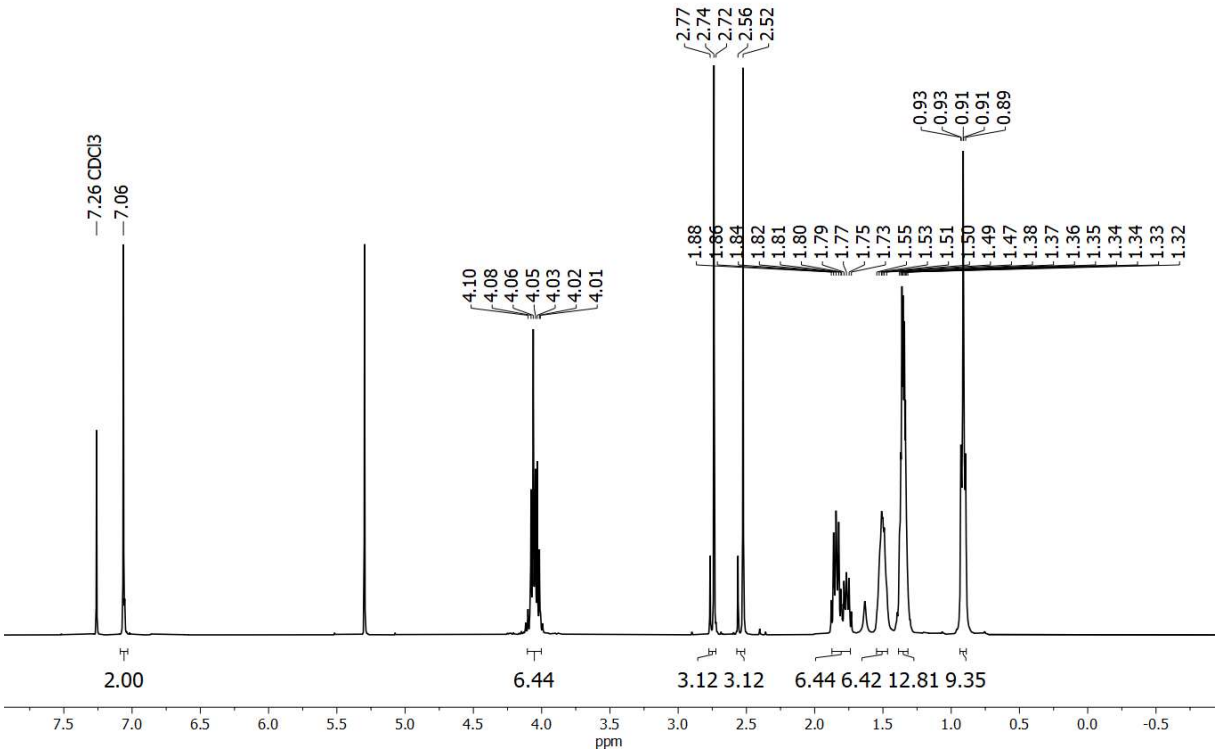


Figure S69. ^{1}H-NMR spectra of compound **3c** dissolved in $CDCl_3$.

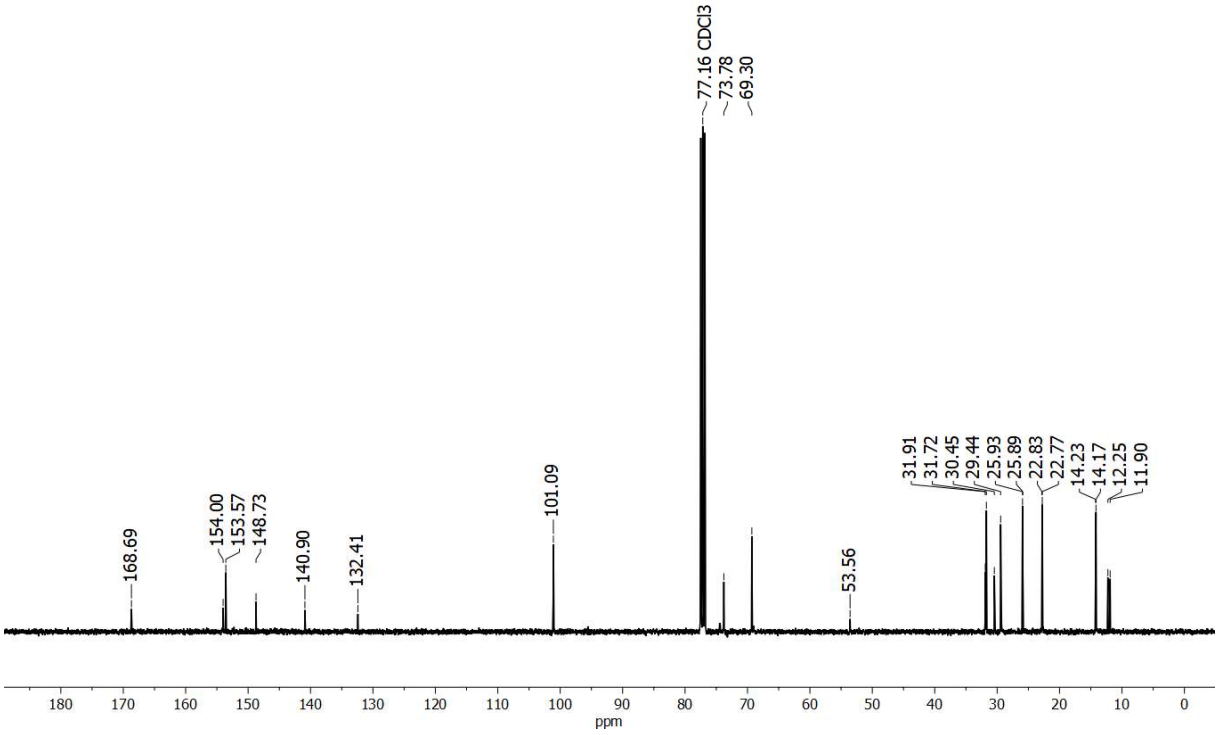


Figure S70. ^{13}C-NMR spectra of compound **3c** dissolved in $CDCl_3$.

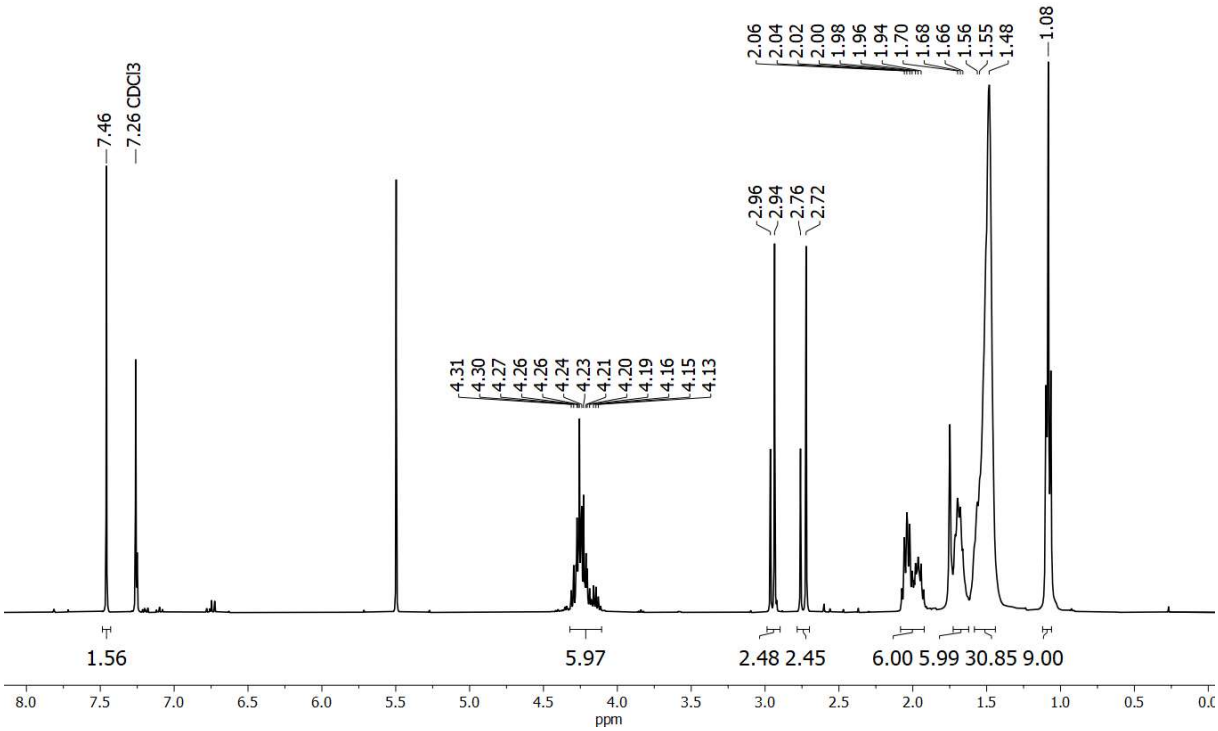


Figure S71. ^{1}H-NMR spectra of compound **3d** dissolved in $CDCl_3$.

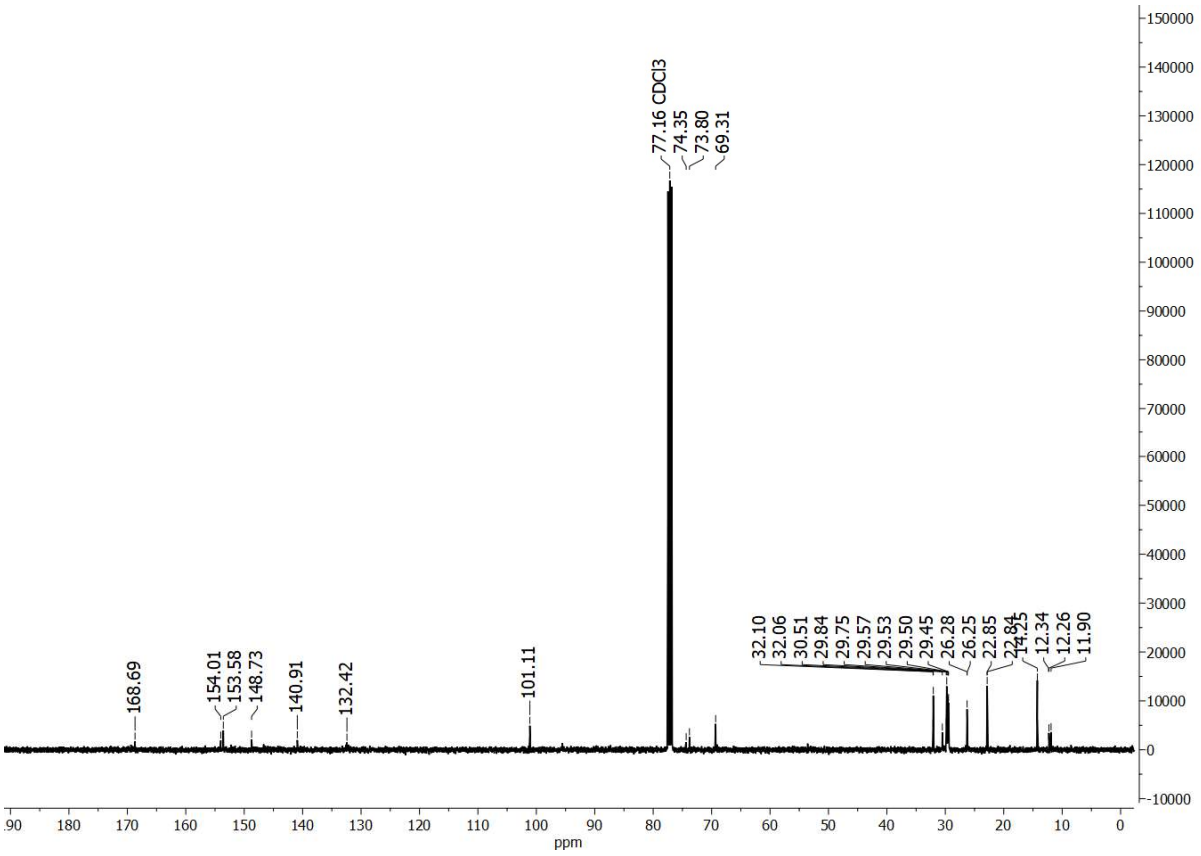


Figure S72. ^{13}C-NMR spectra of compound **3d** dissolved in $CDCl_3$.

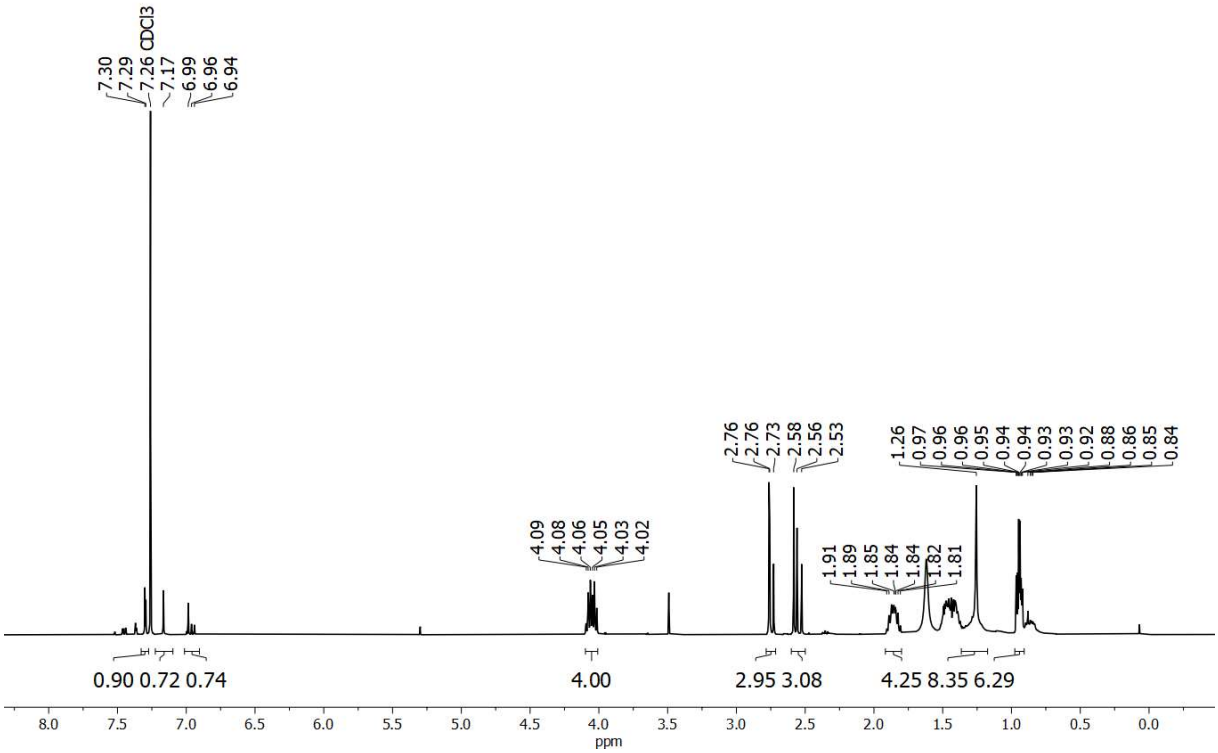


Figure S73. ^{1}H-NMR spectra of compound **2a** dissolved in $CDCl_3$.

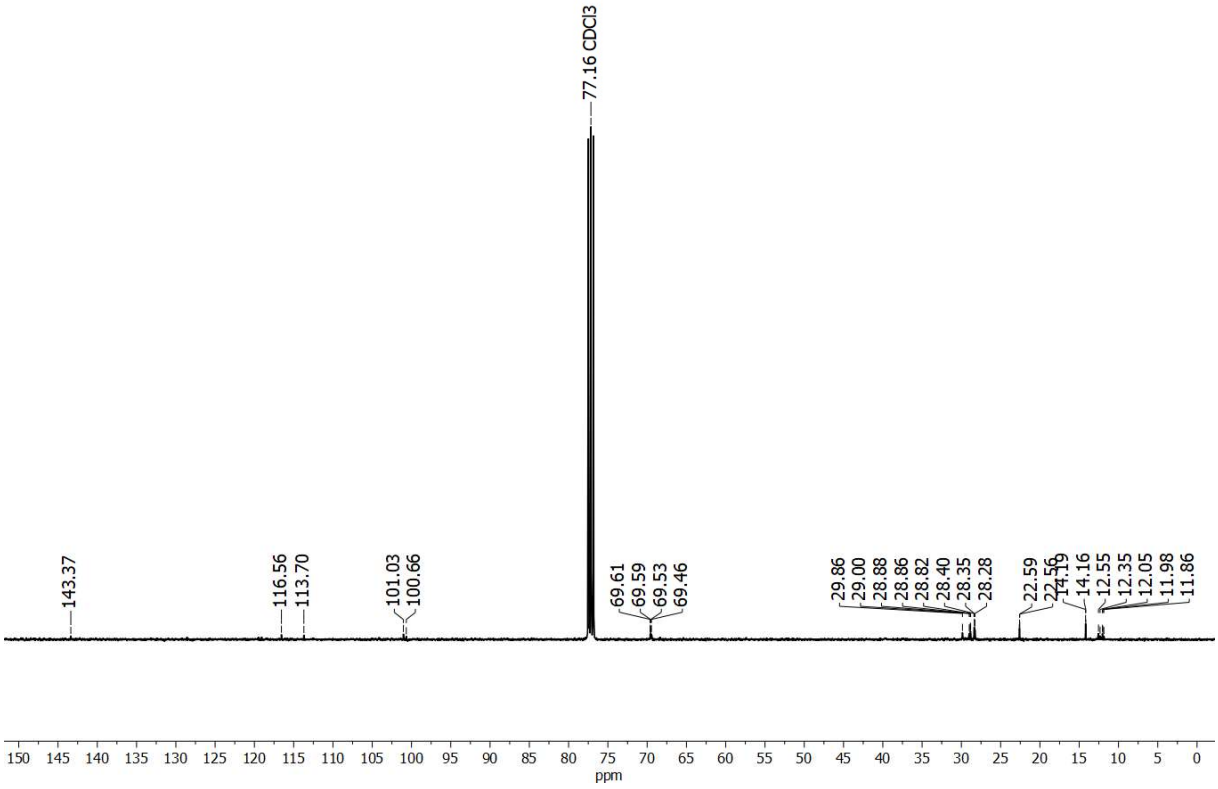


Figure S74. ^{13}C-NMR spectra of compound **2a** dissolved in $CDCl_3$.

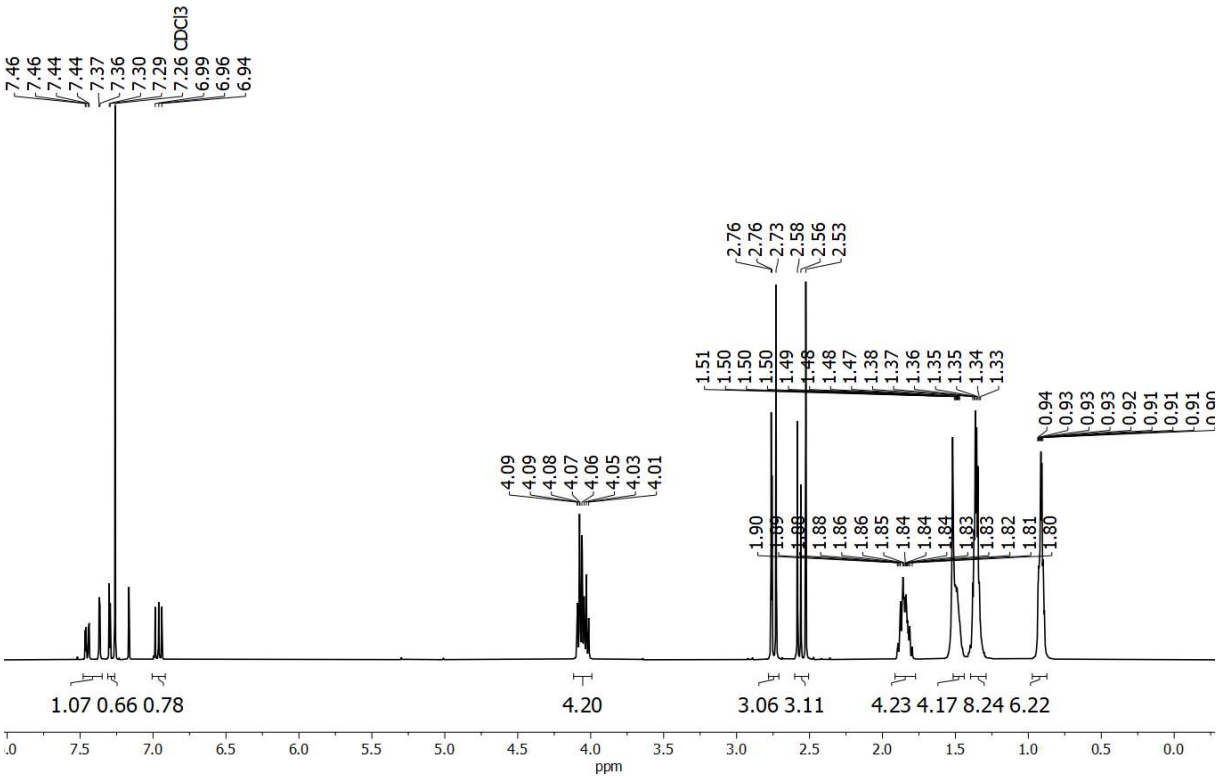


Figure S75. ^{1}H-NMR spectra of compound **2b** dissolved in $CDCl_3$.

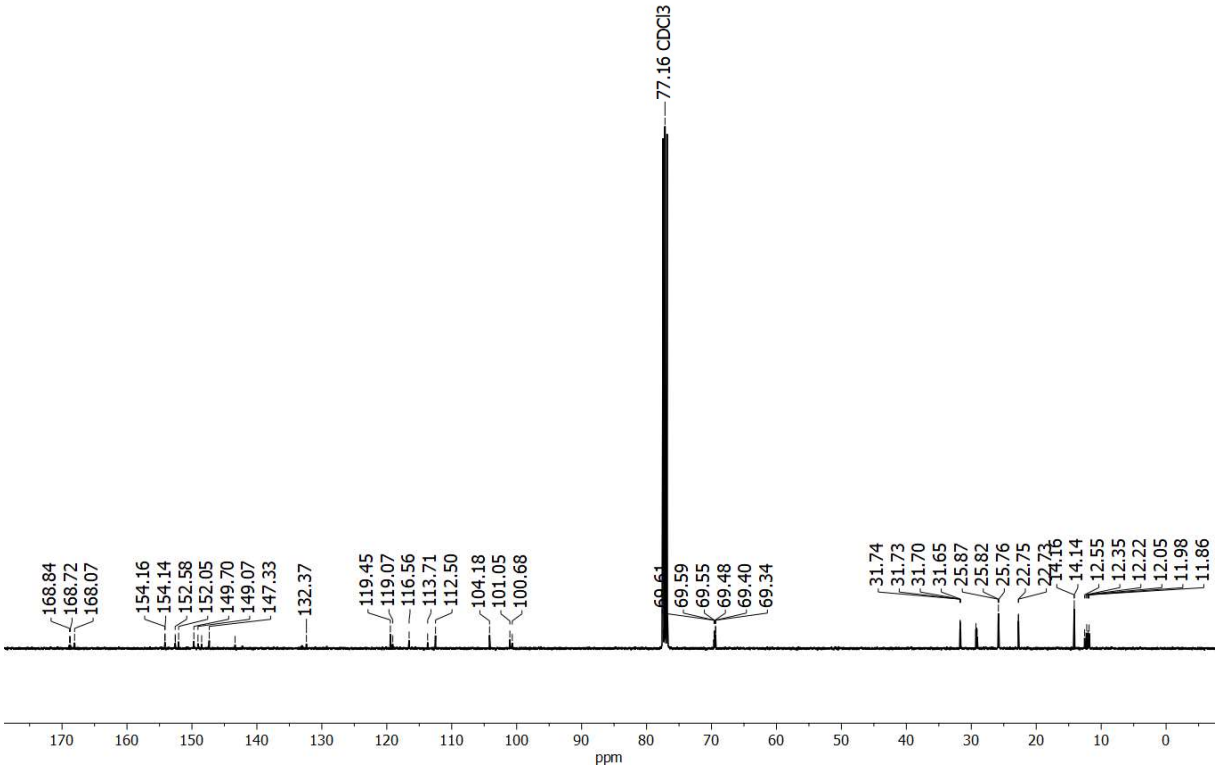


Figure S76. ^{13}C-NMR spectra of compound **2b** dissolved in $CDCl_3$.

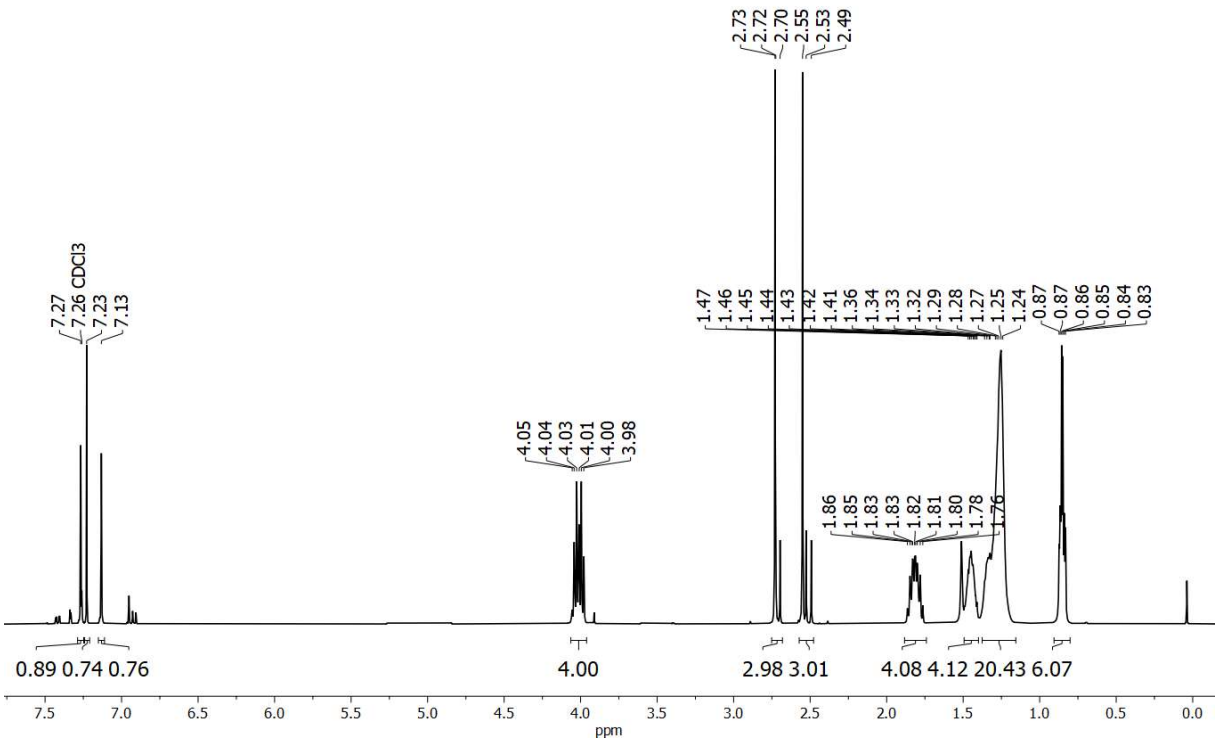


Figure S77. ^{1}H-NMR spectra of compound **2c** dissolved in $CDCl_3$.

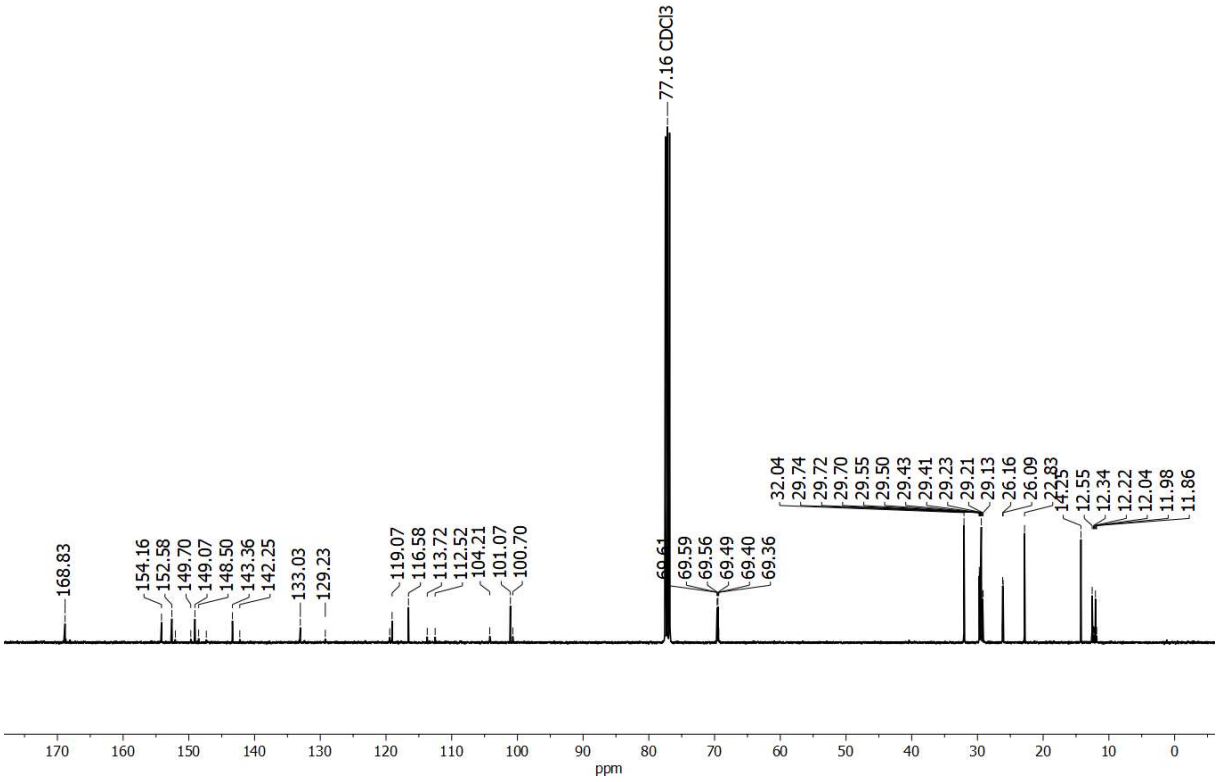


Figure S78. ^{13}C-NMR spectra of compound **2c** dissolved in $CDCl_3$.

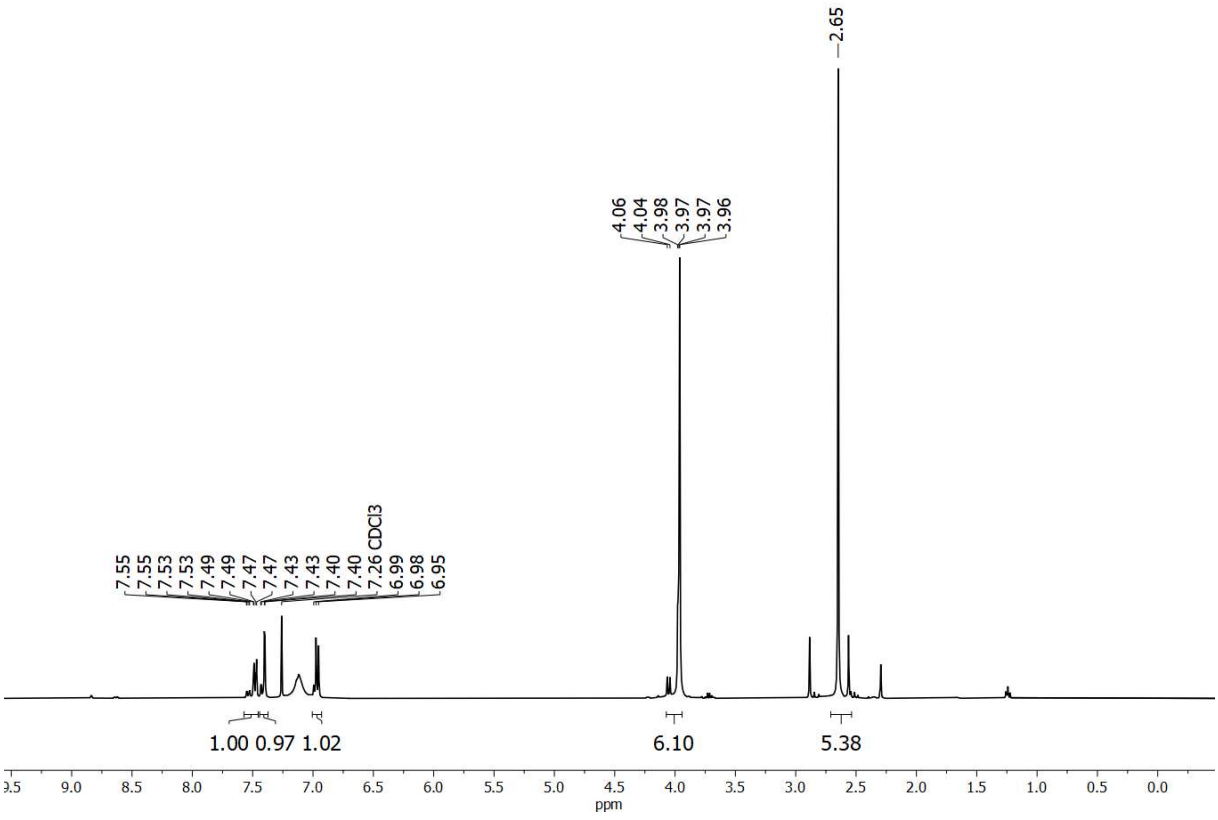


Figure S79. ^{1}H-NMR spectra of compound **2d** dissolved in $CDCl_3$.

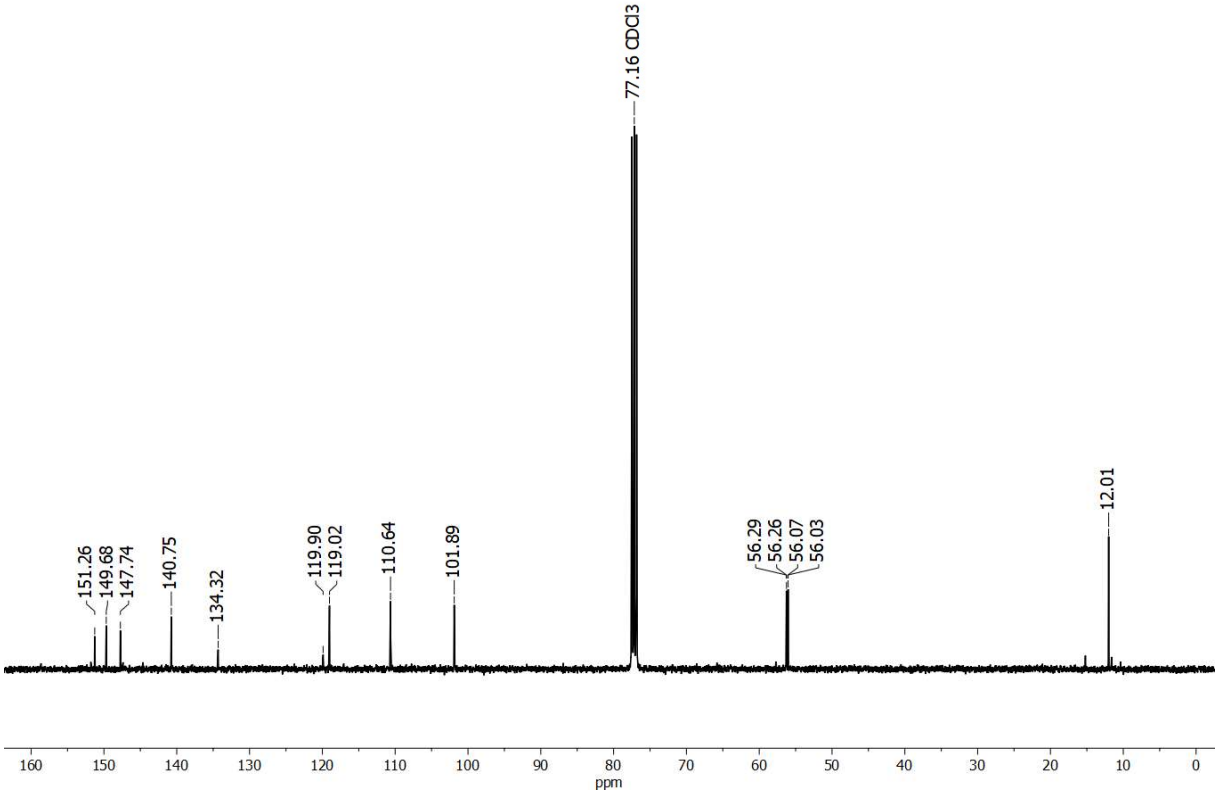


Figure S80. ^{13}C-NMR spectra of compound **2d** dissolved in $CDCl_3$.

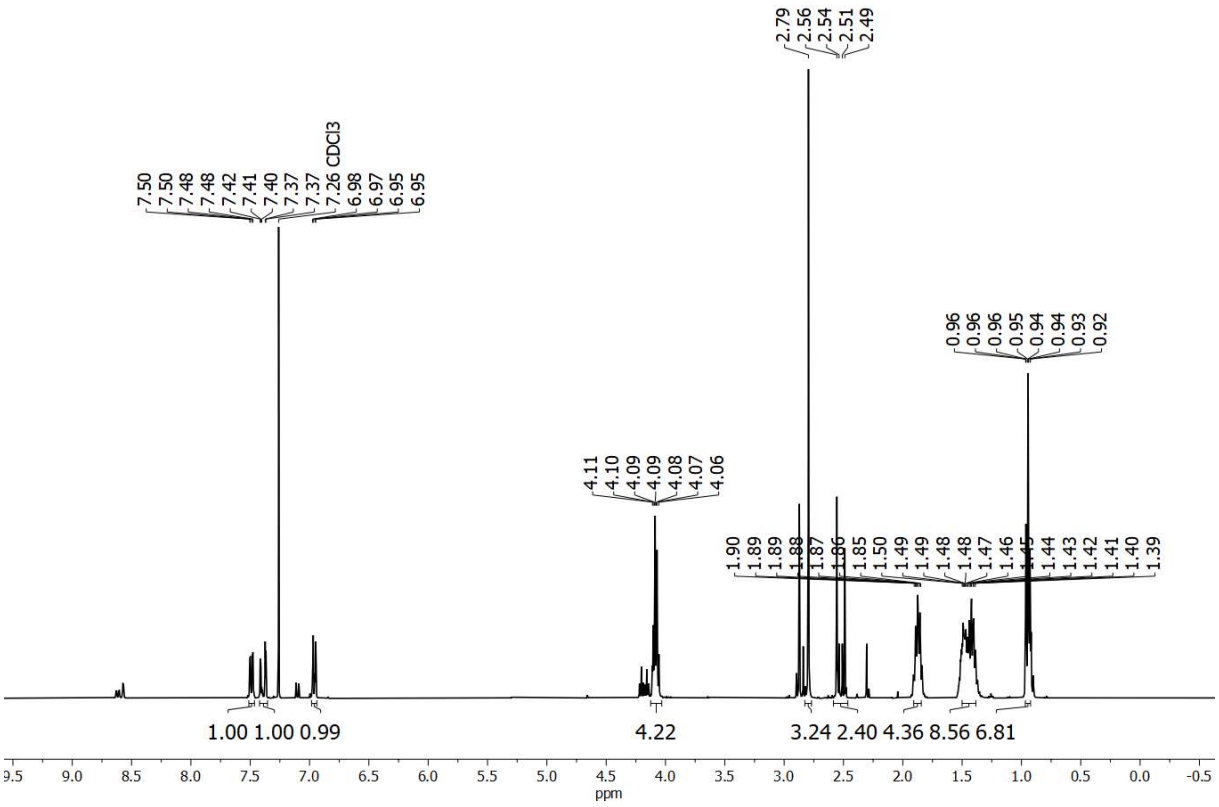


Figure S81. ^{1}H-NMR spectra of compound **2e** dissolved in $CDCl_3$.

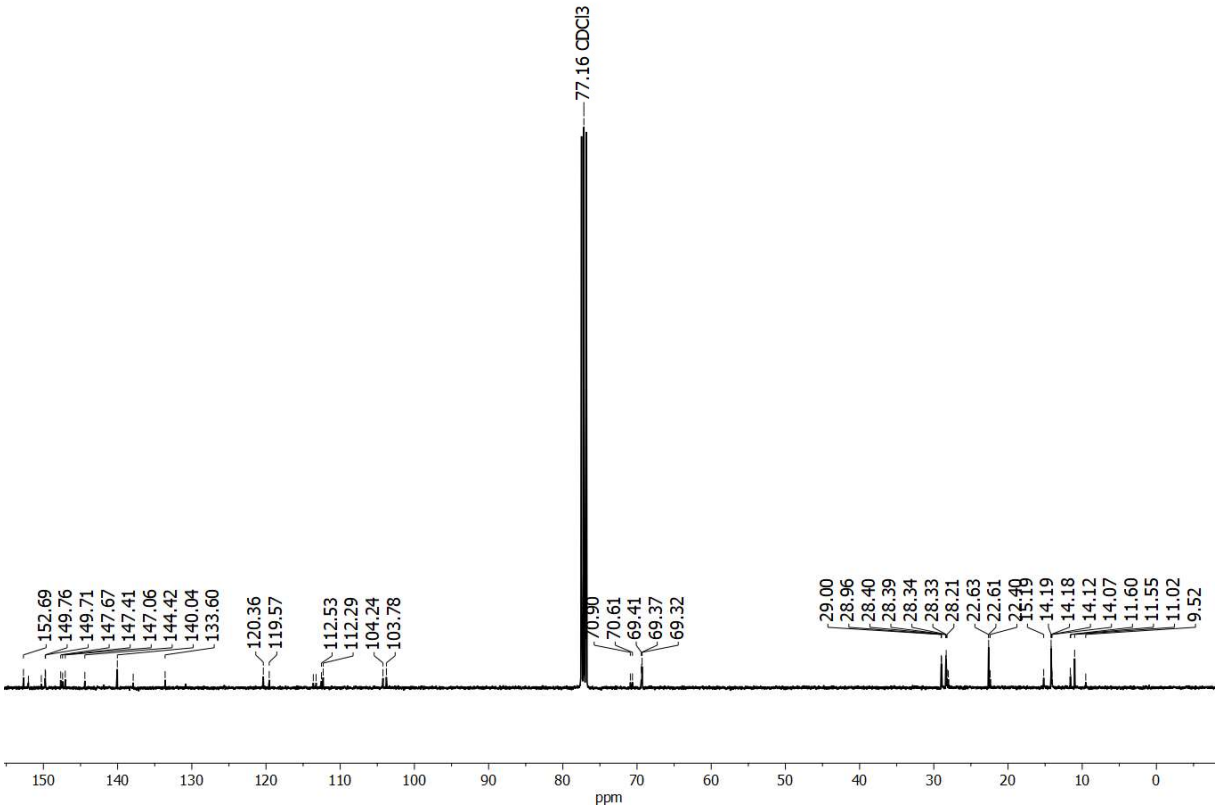


Figure S82. ^{13}C-NMR spectra of compound **2e** dissolved in $CDCl_3$.

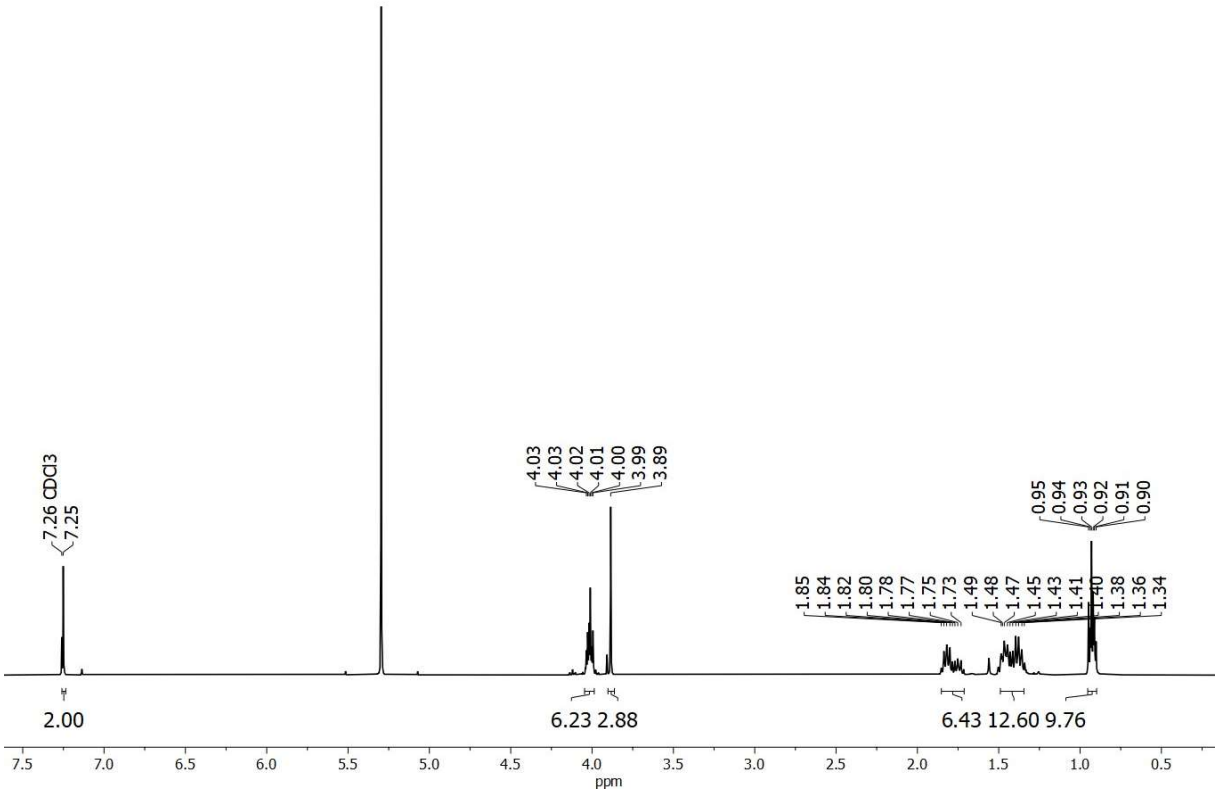


Figure S83. ^{1}H-NMR spectra of compound **31b** dissolved in $CDCl_3$.

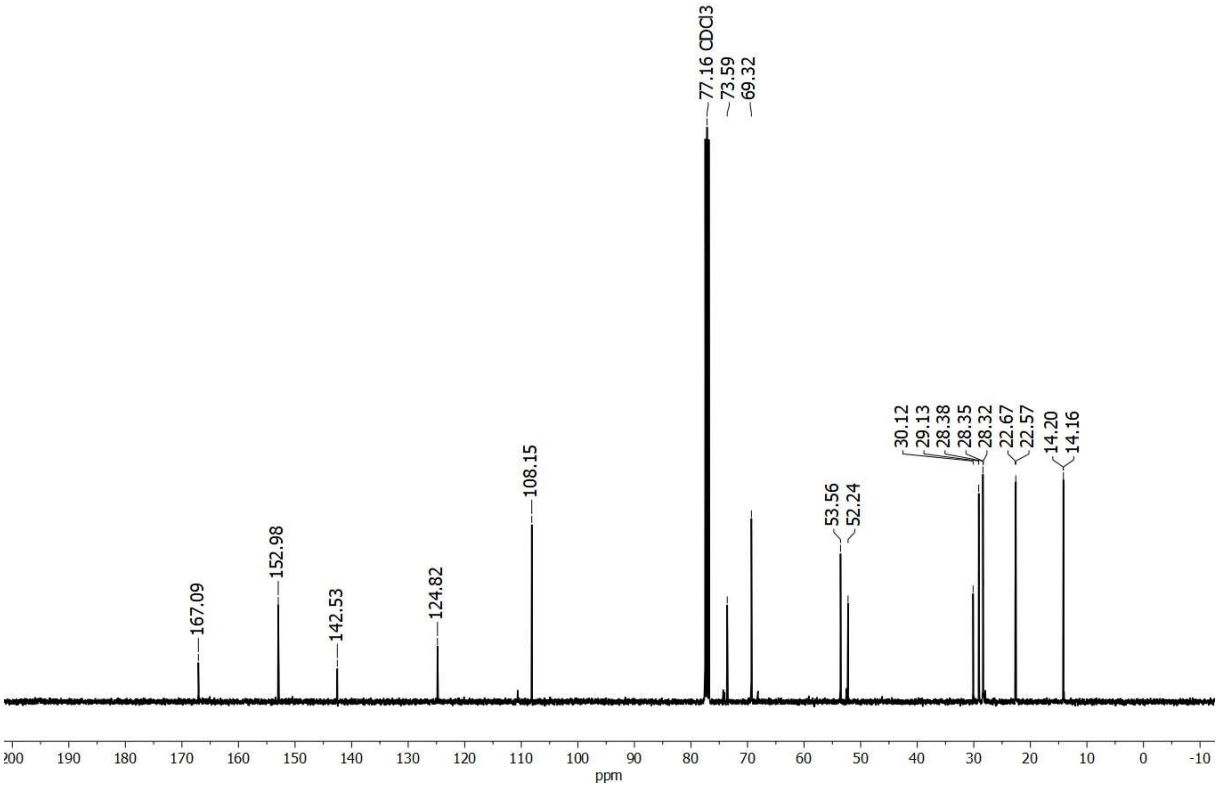


Figure S84. ^{13}C-NMR spectra of compound **31b** dissolved in $CDCl_3$.

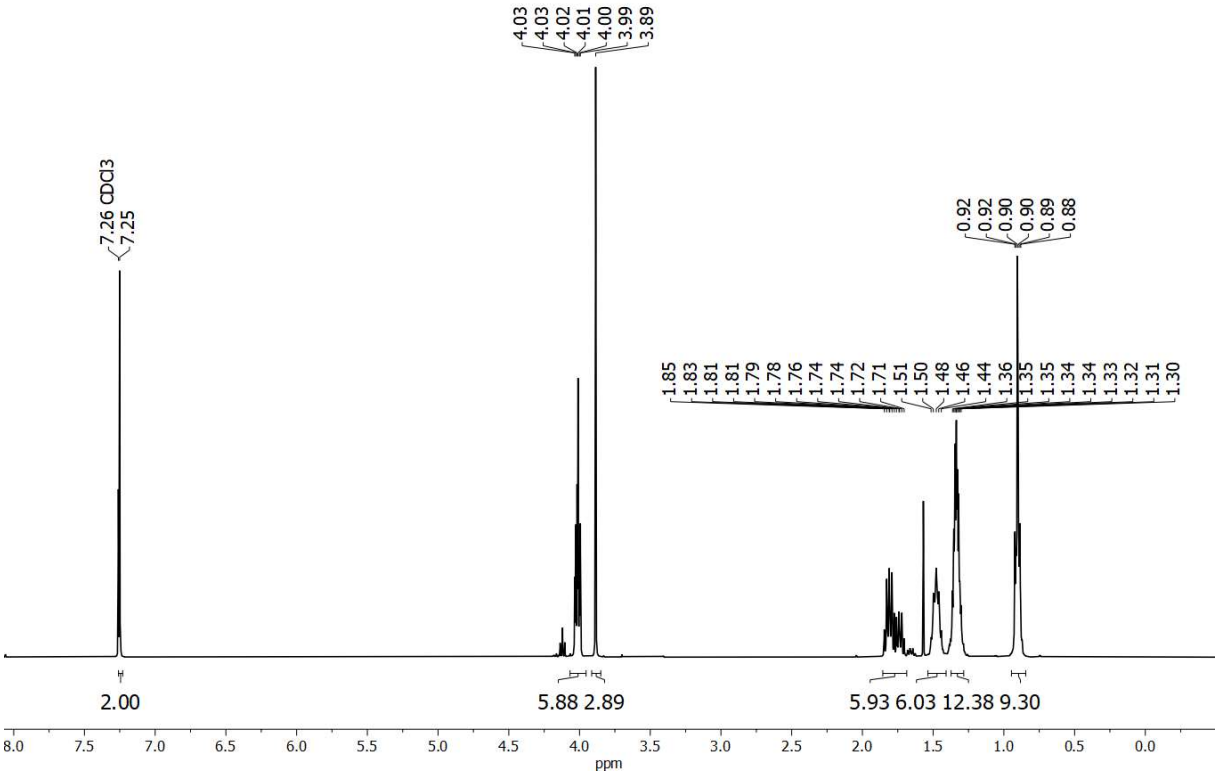


Figure S85. ^{1}H-NMR spectra of compound **31c** dissolved in $CDCl_3$.

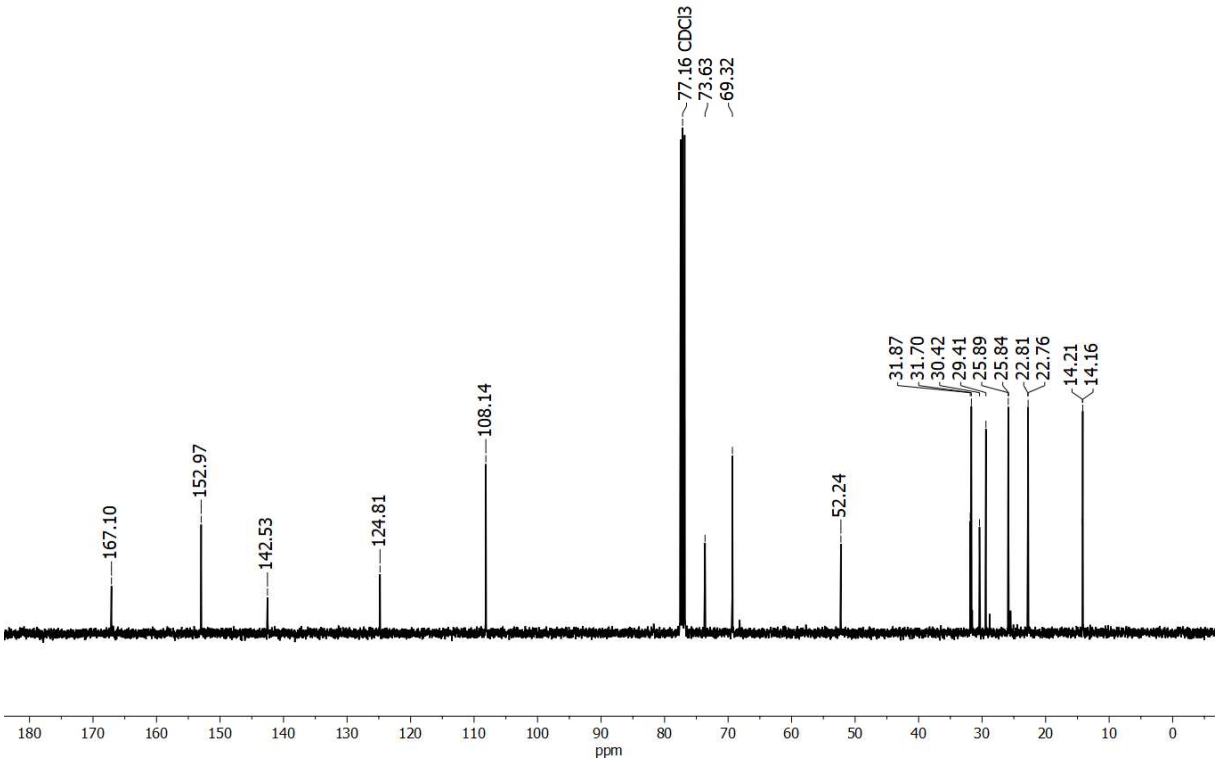


Figure S86. ^{13}C-NMR spectra of compound **31c** dissolved in $CDCl_3$.

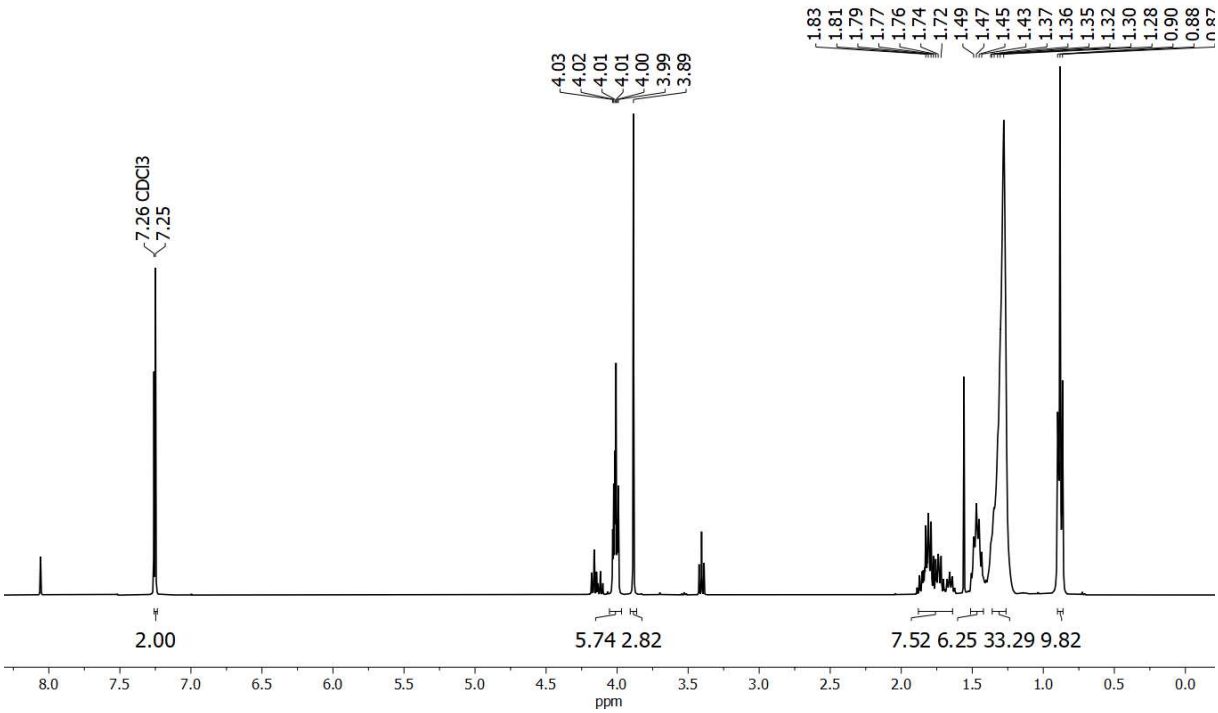


Figure S87. ^{1}H-NMR spectra of compound **31d** dissolved in $CDCl_3$.

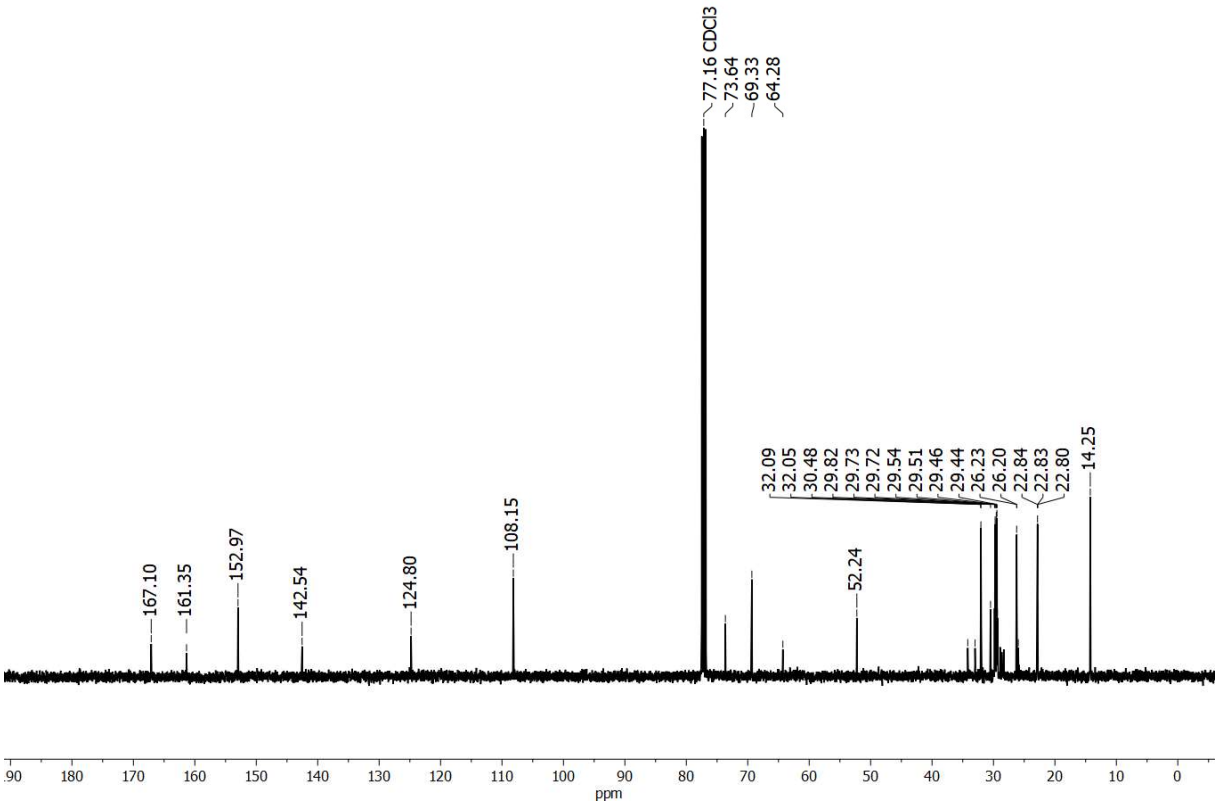


Figure S88. ^{13}C-NMR spectra of compound **31d** dissolved in $CDCl_3$.

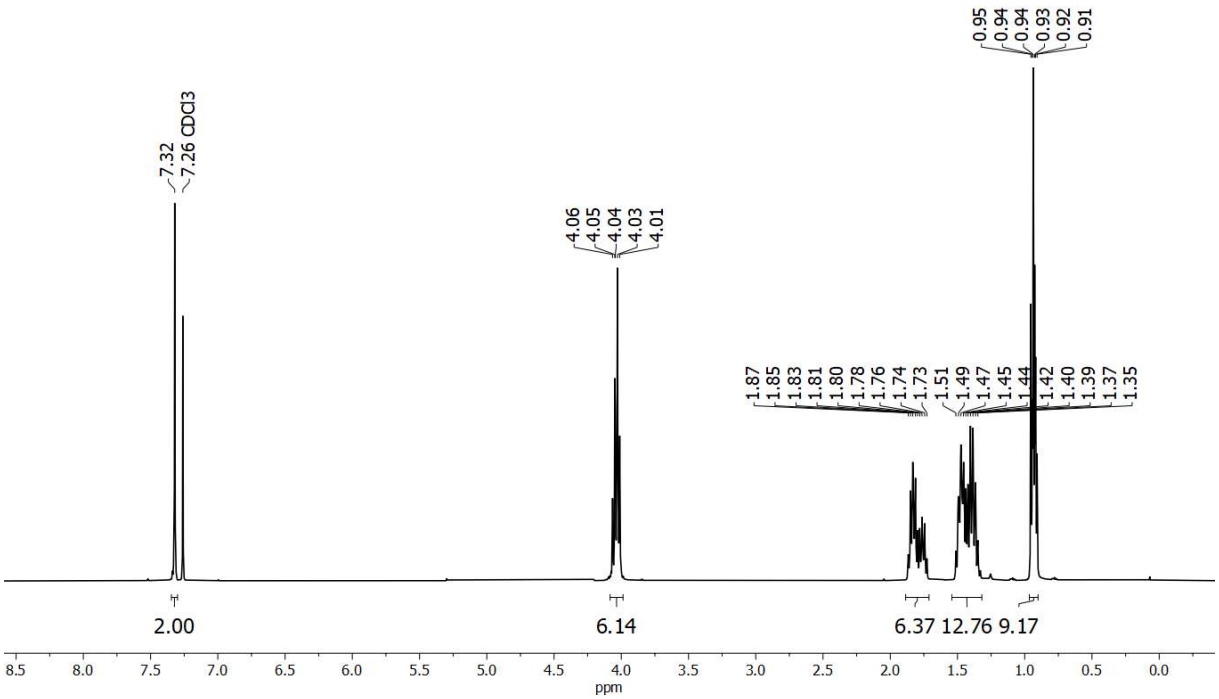


Figure S89. ^{1}H-NMR spectra of compound **32b** dissolved in $CDCl_3$.

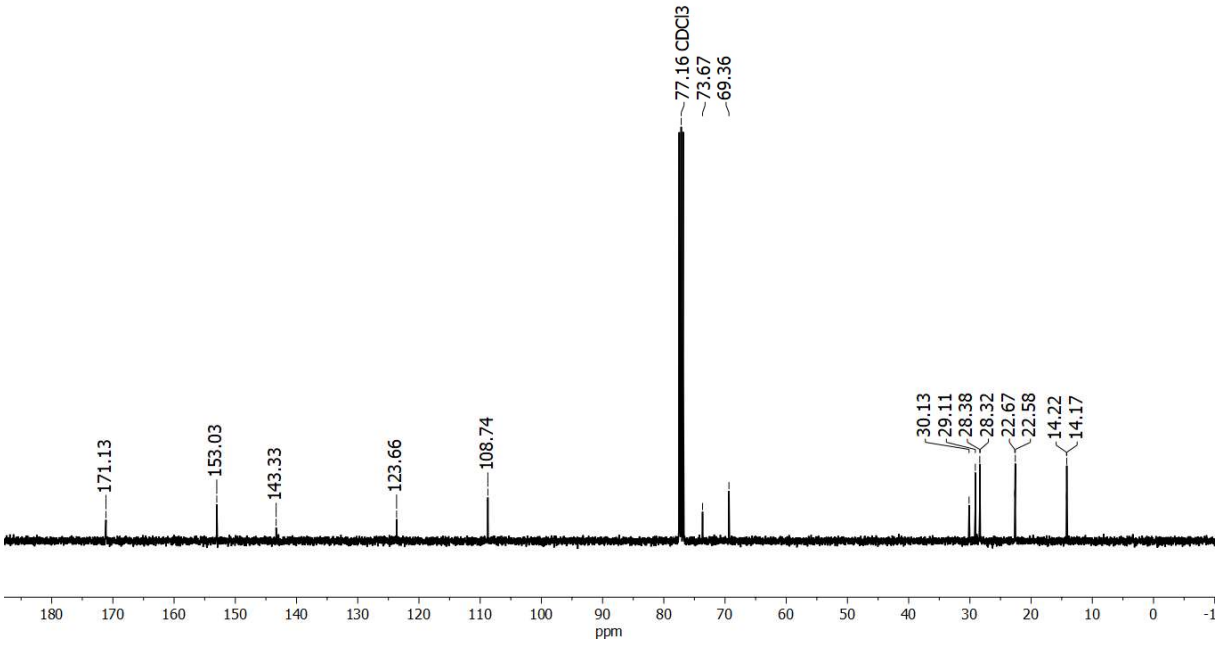


Figure S90. ^{13}C-NMR spectra of compound **32b** dissolved in $CDCl_3$.

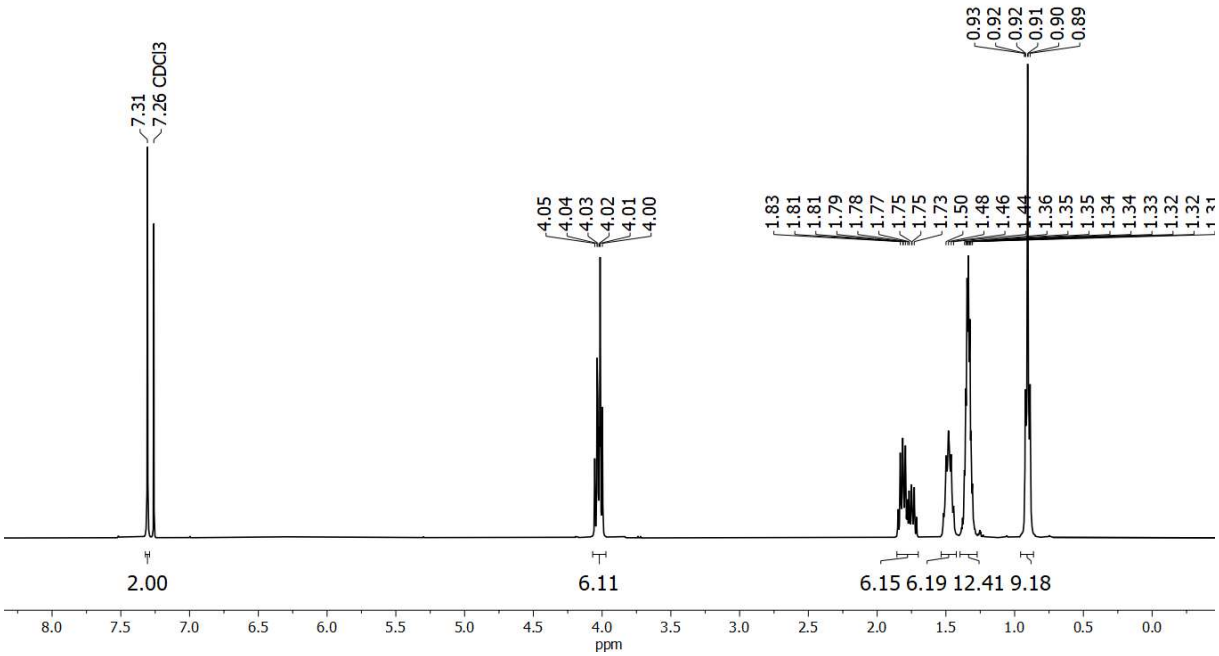


Figure S91. ^{1}H-NMR spectra of compound **32c** dissolved in $CDCl_3$.

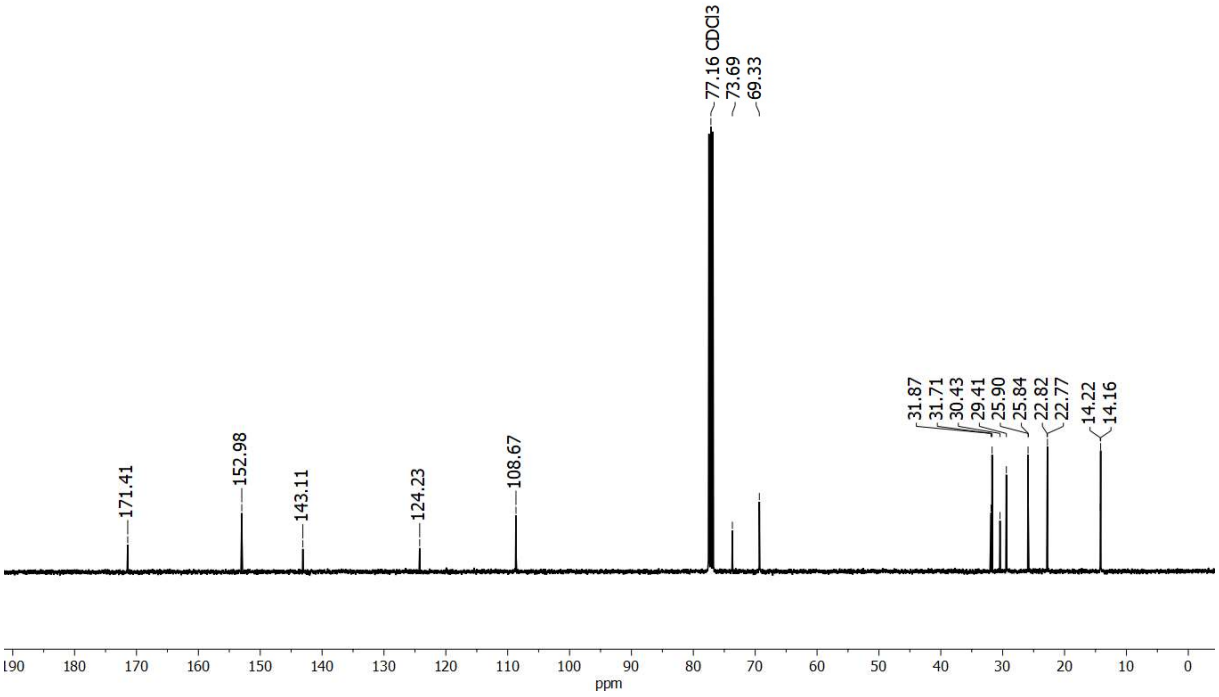


Figure S92. ^{13}C-NMR spectra of compound **32c** dissolved in $CDCl_3$.

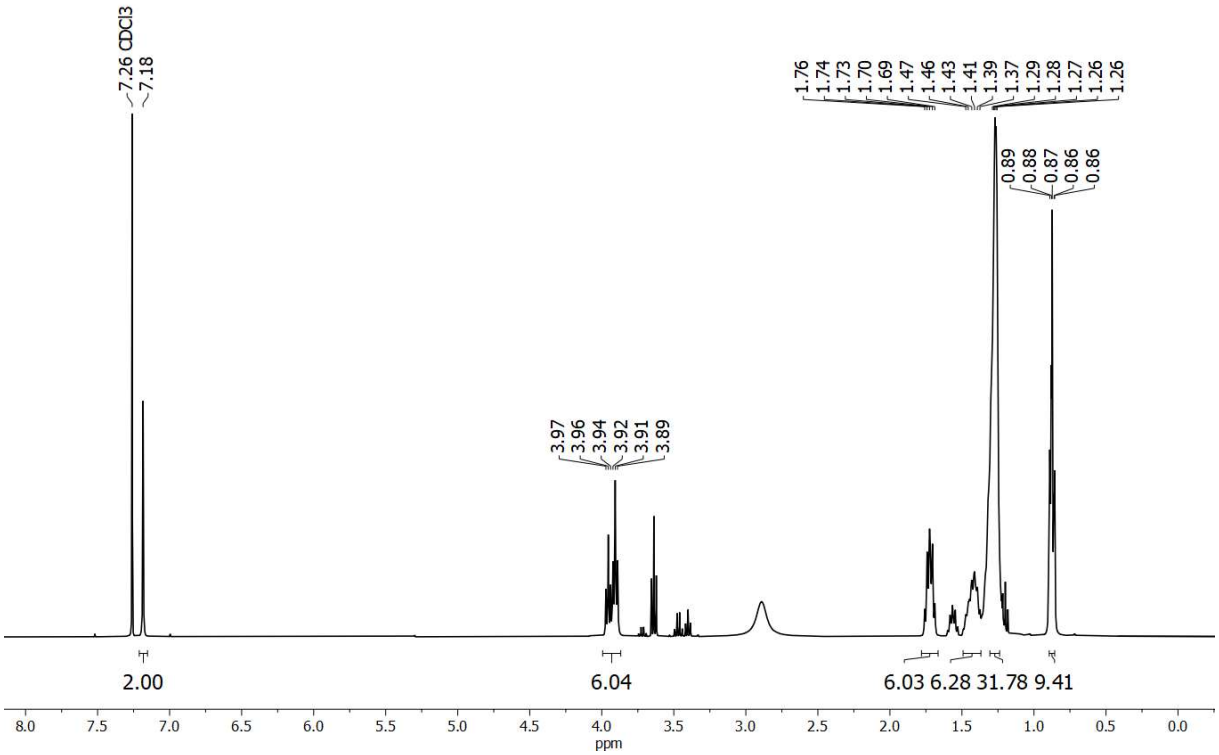


Figure S93. ^{1}H-NMR spectra of compound **32d** dissolved in $CDCl_3$.

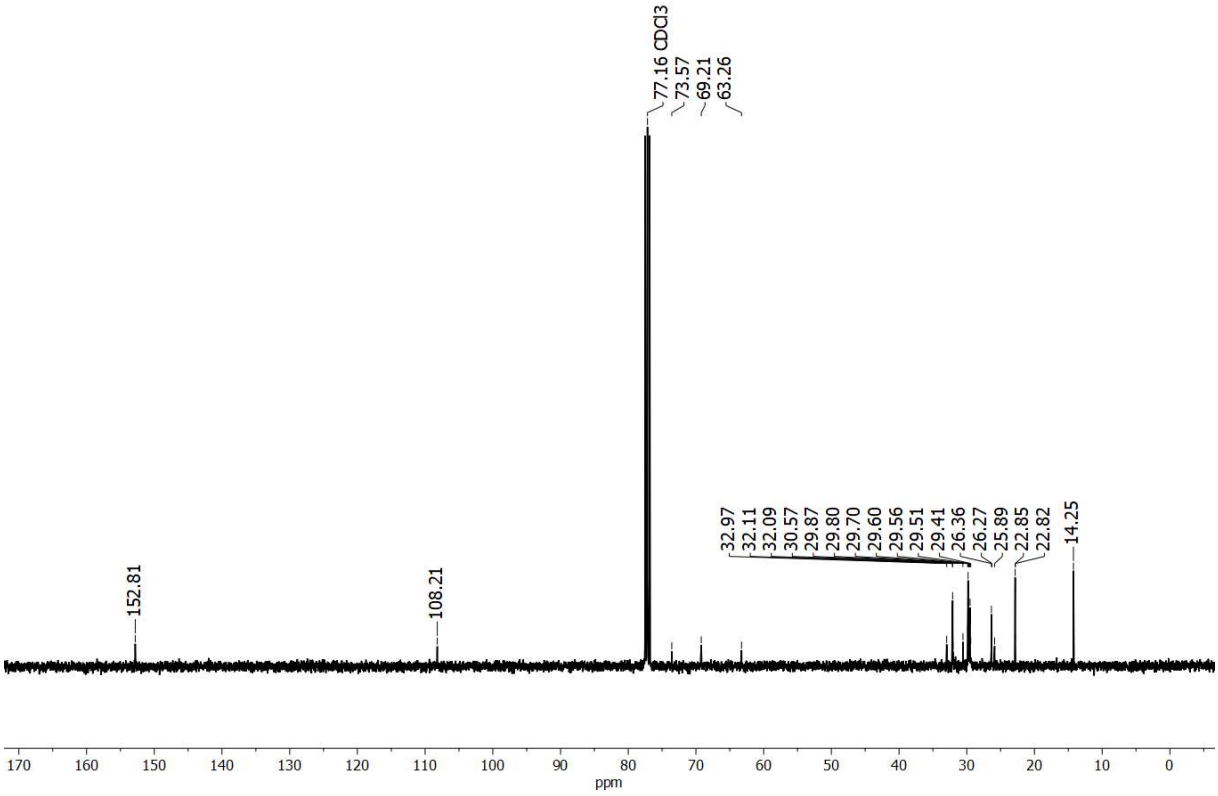


Figure S94. ^{13}C-NMR spectra of compound **32d** dissolved in $CDCl_3$.

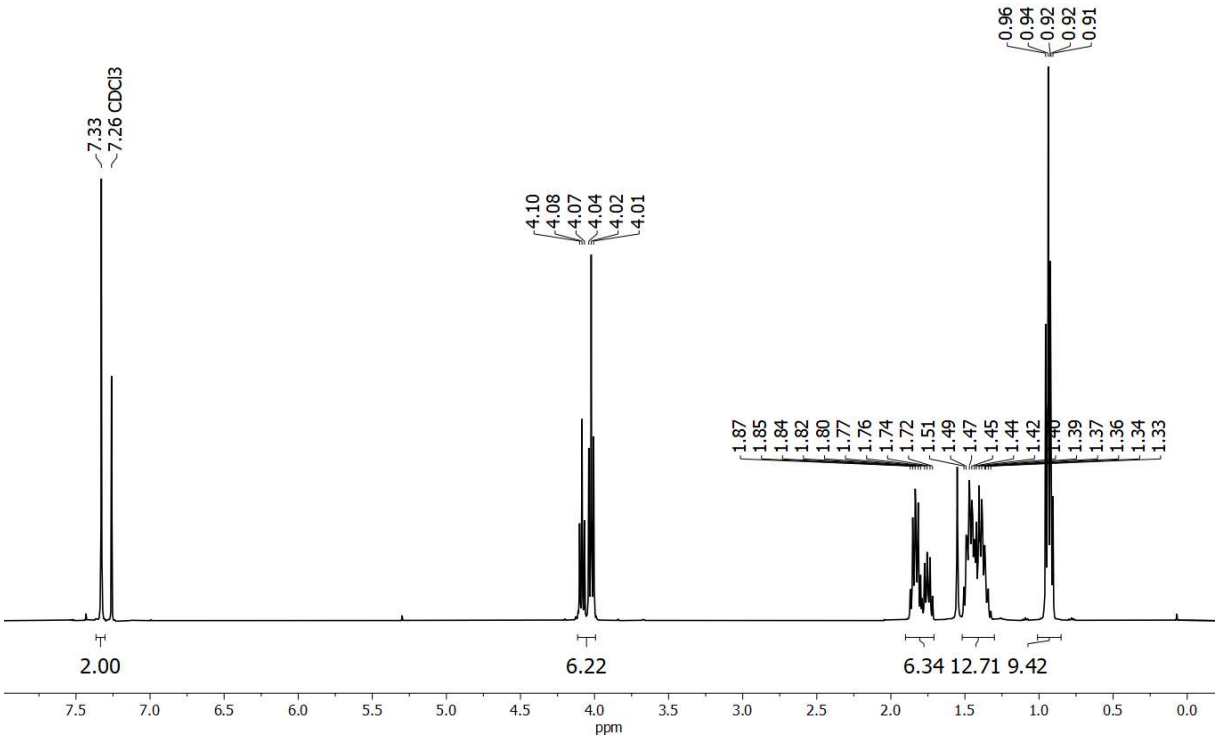


Figure S95. ^{1}H-NMR spectra of compound **33b** dissolved in $CDCl_3$.

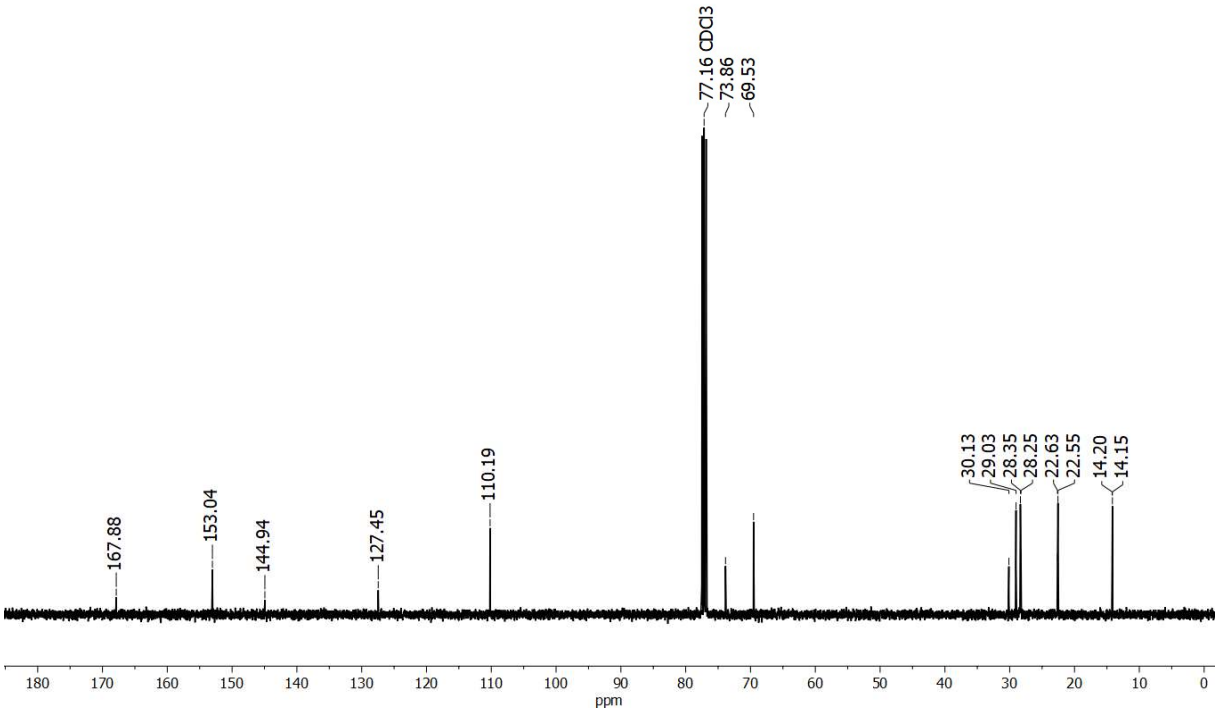


Figure S96. ^{13}C-NMR spectra of compound **33b** dissolved in $CDCl_3$.

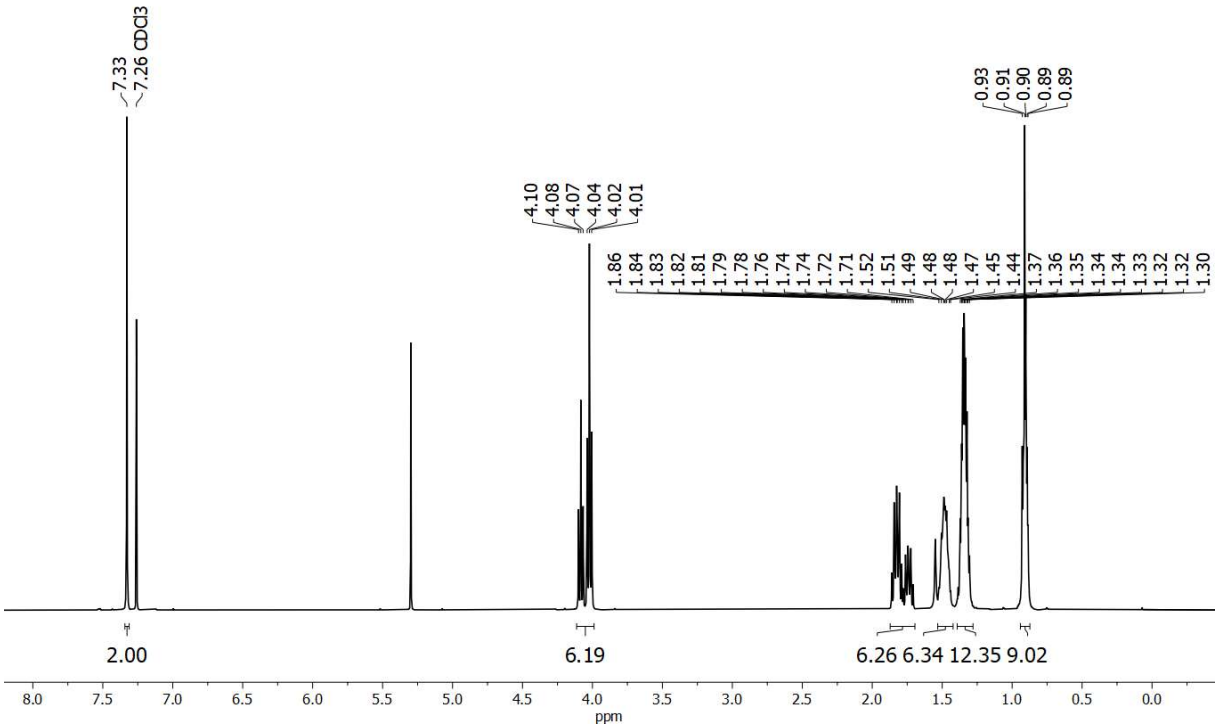


Figure S97. ^{1}H-NMR spectra of compound **33c** dissolved in $CDCl_3$.

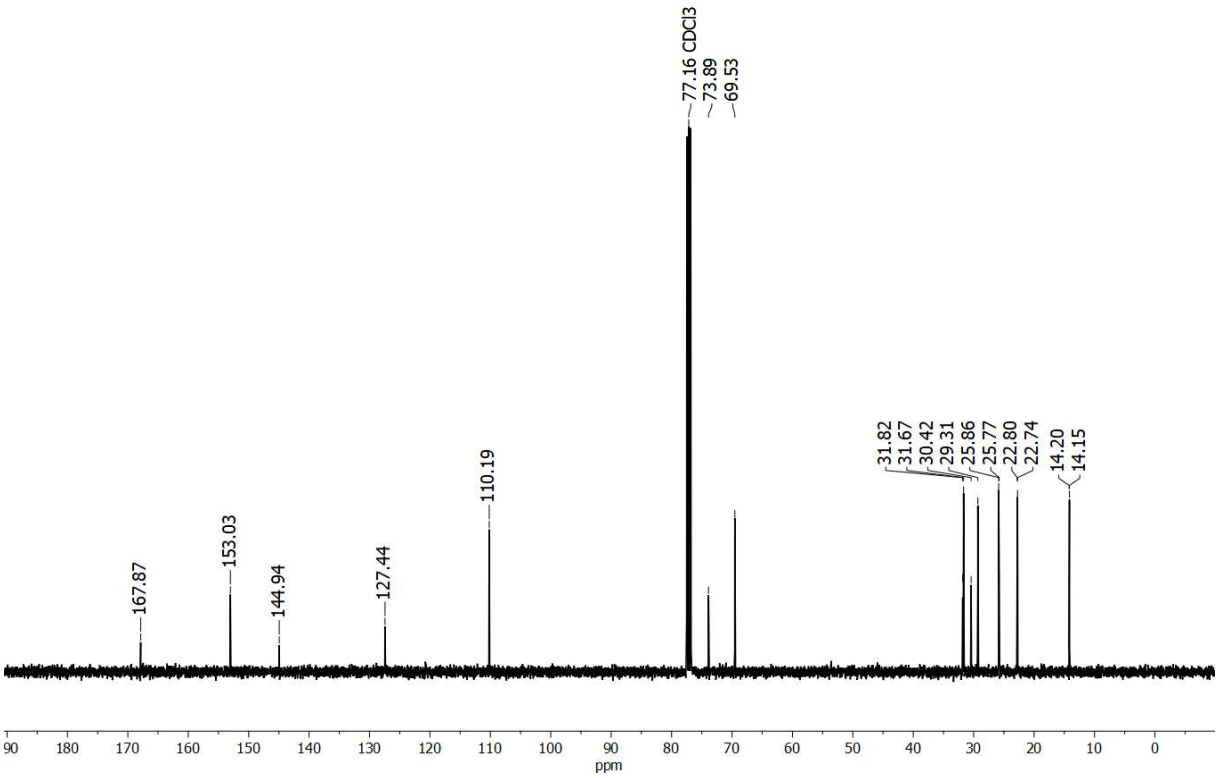


Figure S98. ^{13}C-NMR spectra of compound **33c** dissolved in $CDCl_3$.

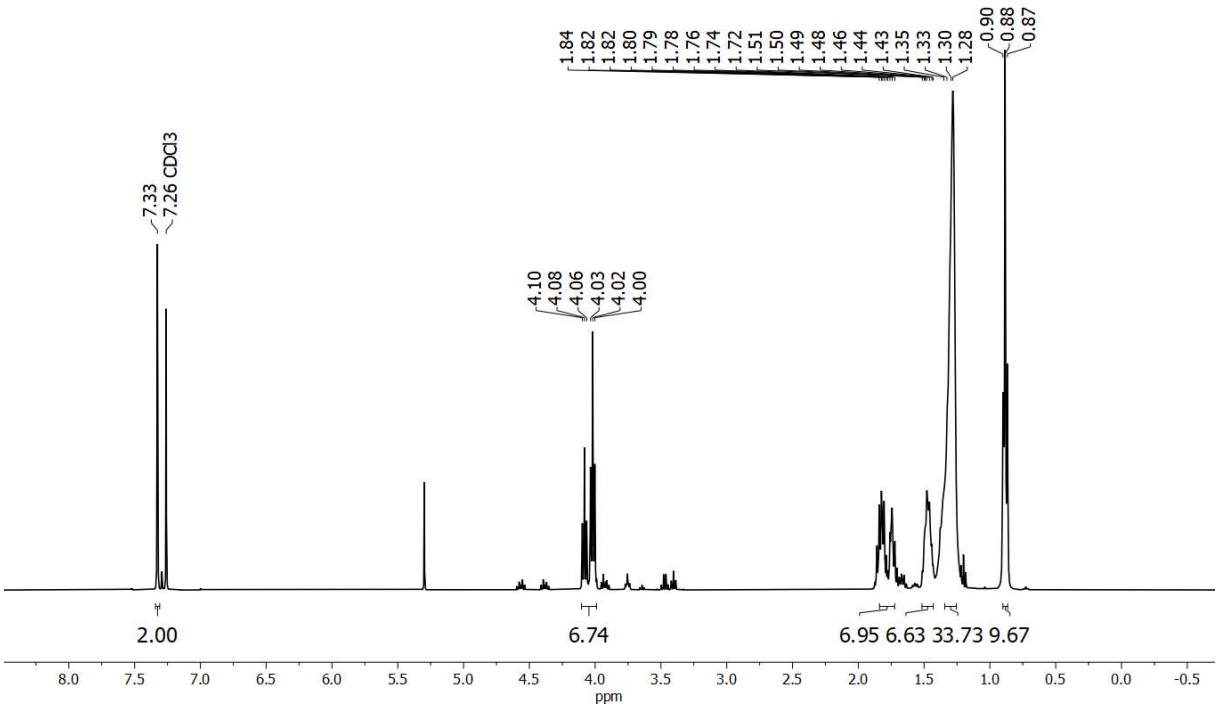


Figure S99. ^{1}H-NMR spectra of compound **33d** dissolved in $CDCl_3$.

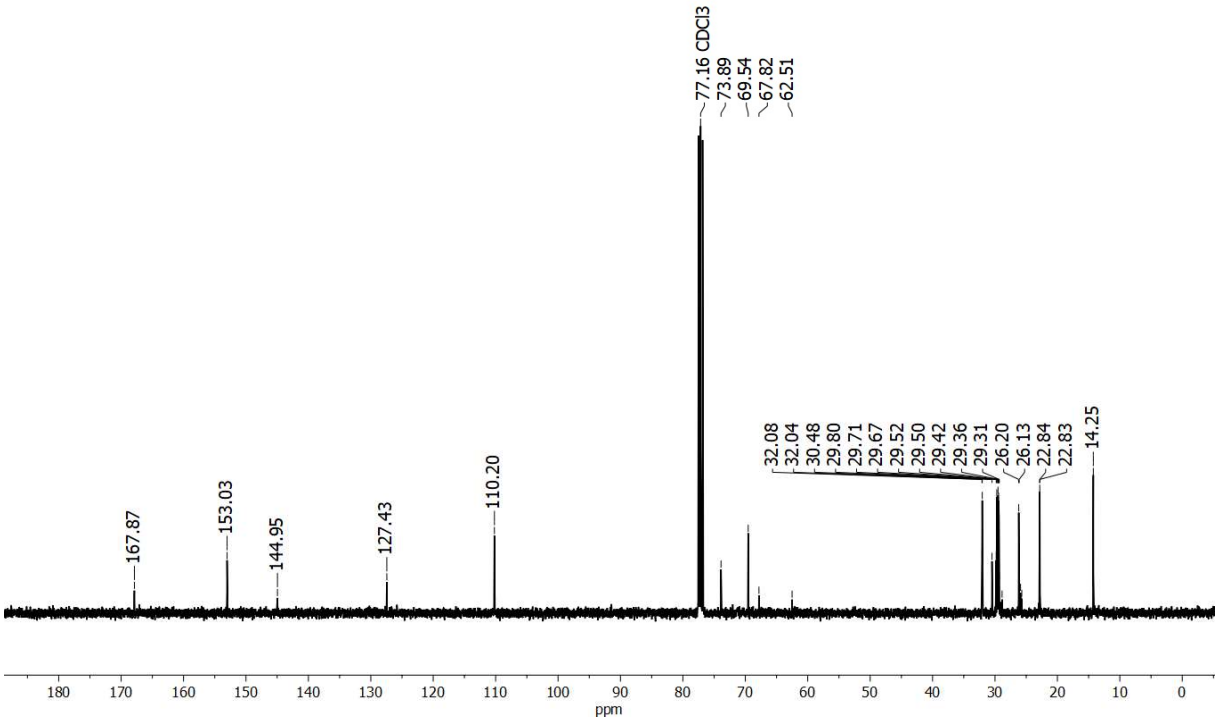


Figure S100. ^{13}C-NMR spectra of compound **33d** dissolved in $CDCl_3$.

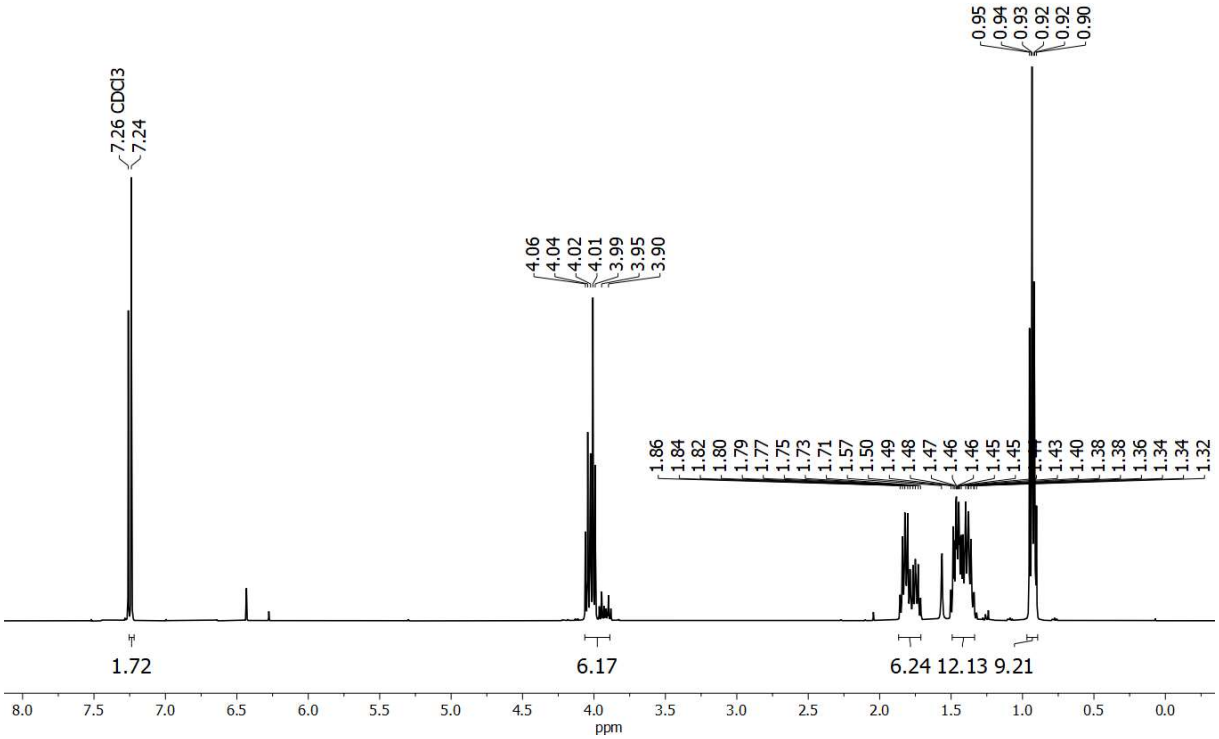


Figure S101. ^{1}H-NMR spectra of compound **34b** dissolved in $CDCl_3$.

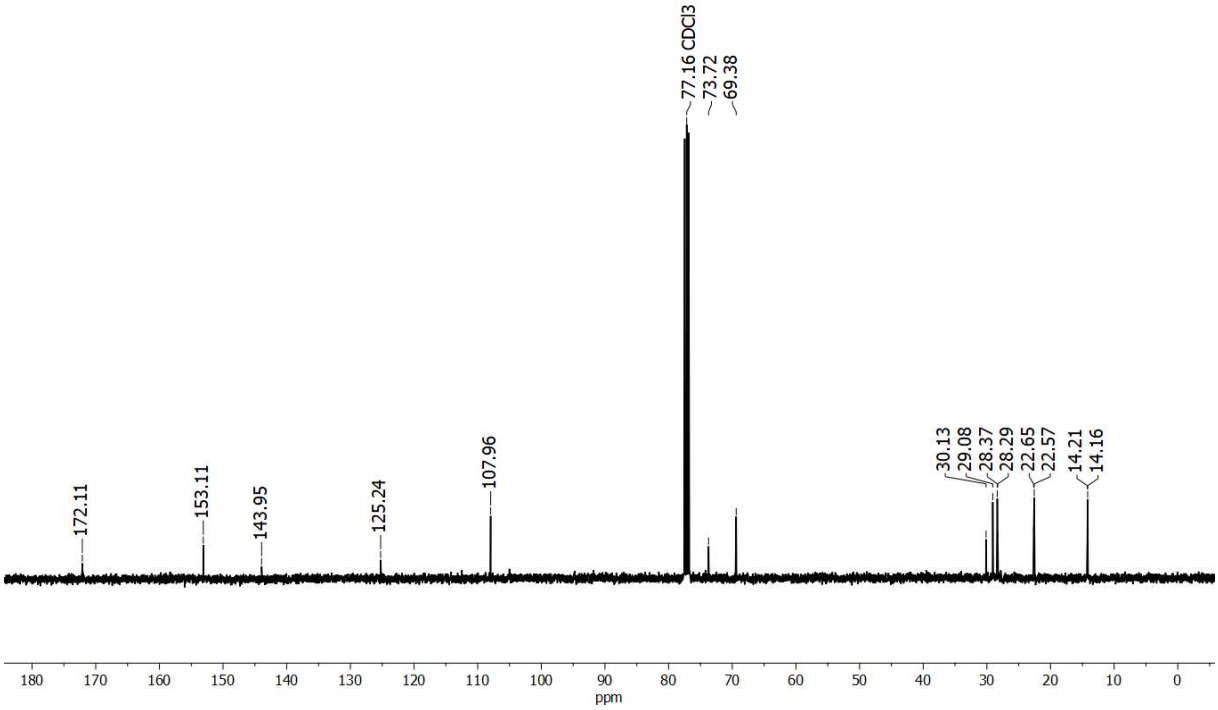


Figure S102. ^{13}C-NMR spectra of compound **34b** dissolved in $CDCl_3$.

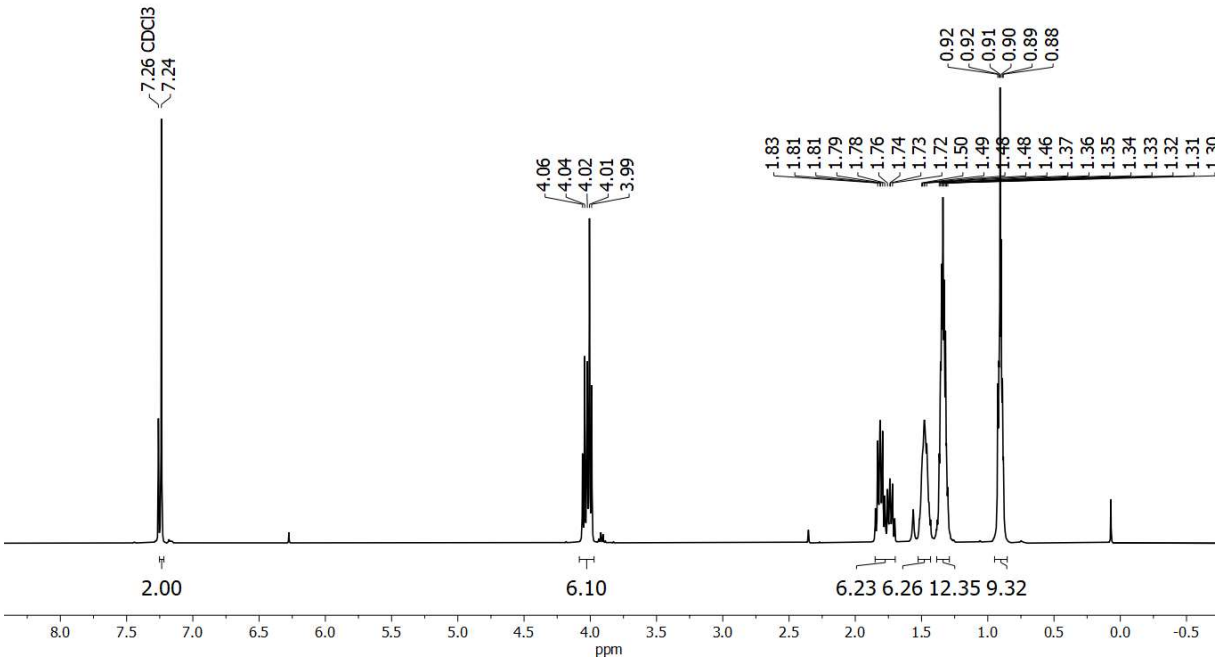


Figure S103. ^{1}H-NMR spectra of compound **34c** dissolved in $CDCl_3$.

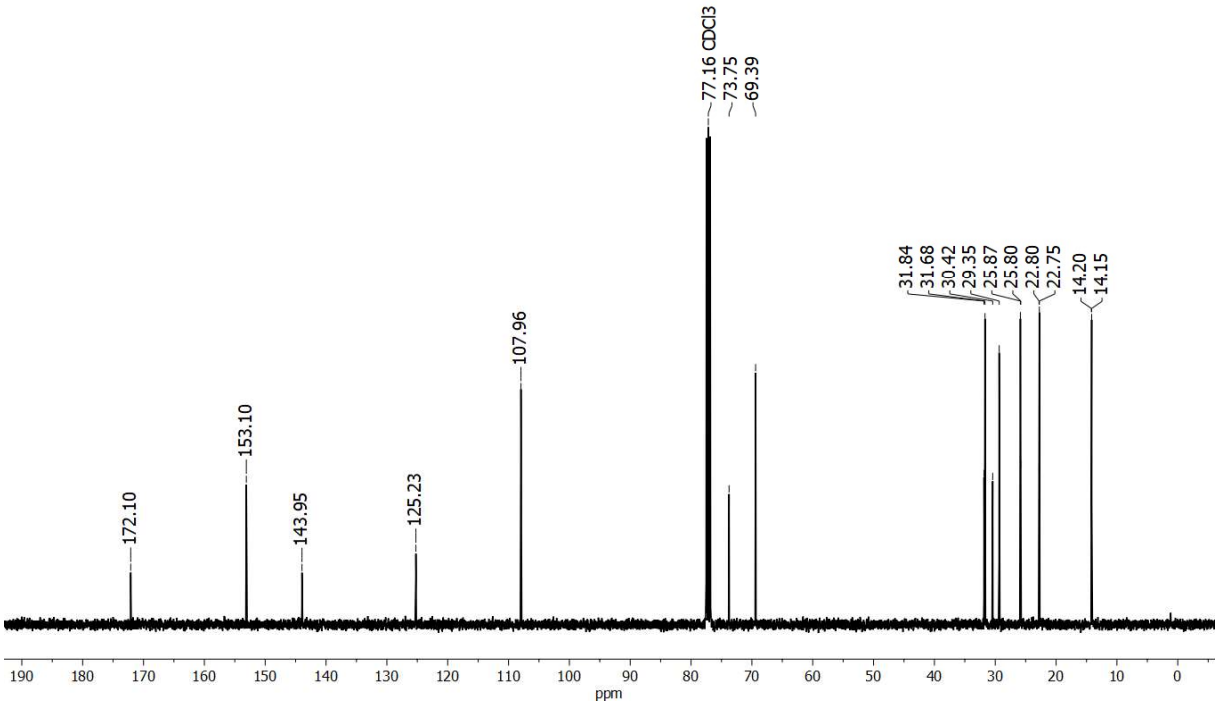


Figure S104. ^{13}C-NMR spectra of compound **34c** dissolved in $CDCl_3$.

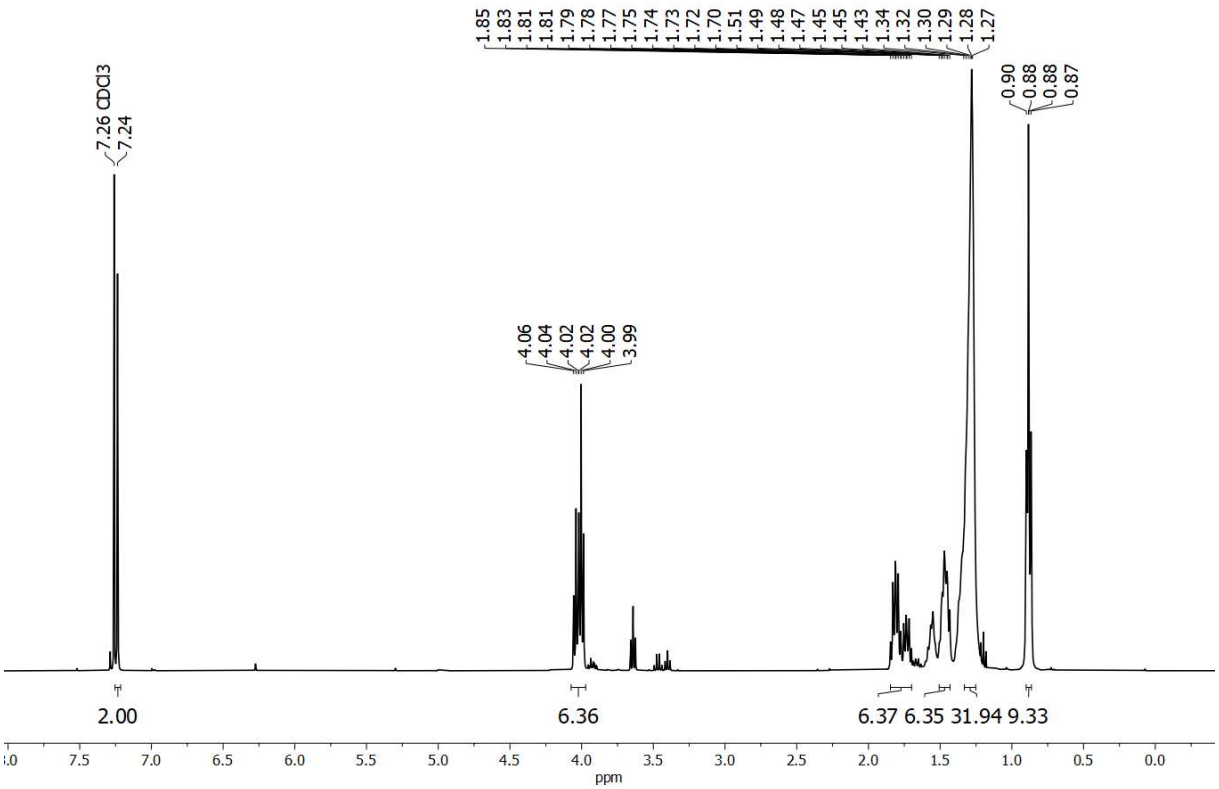


Figure S105. ^{1}H-NMR spectra of compound **34d** dissolved in $CDCl_3$.

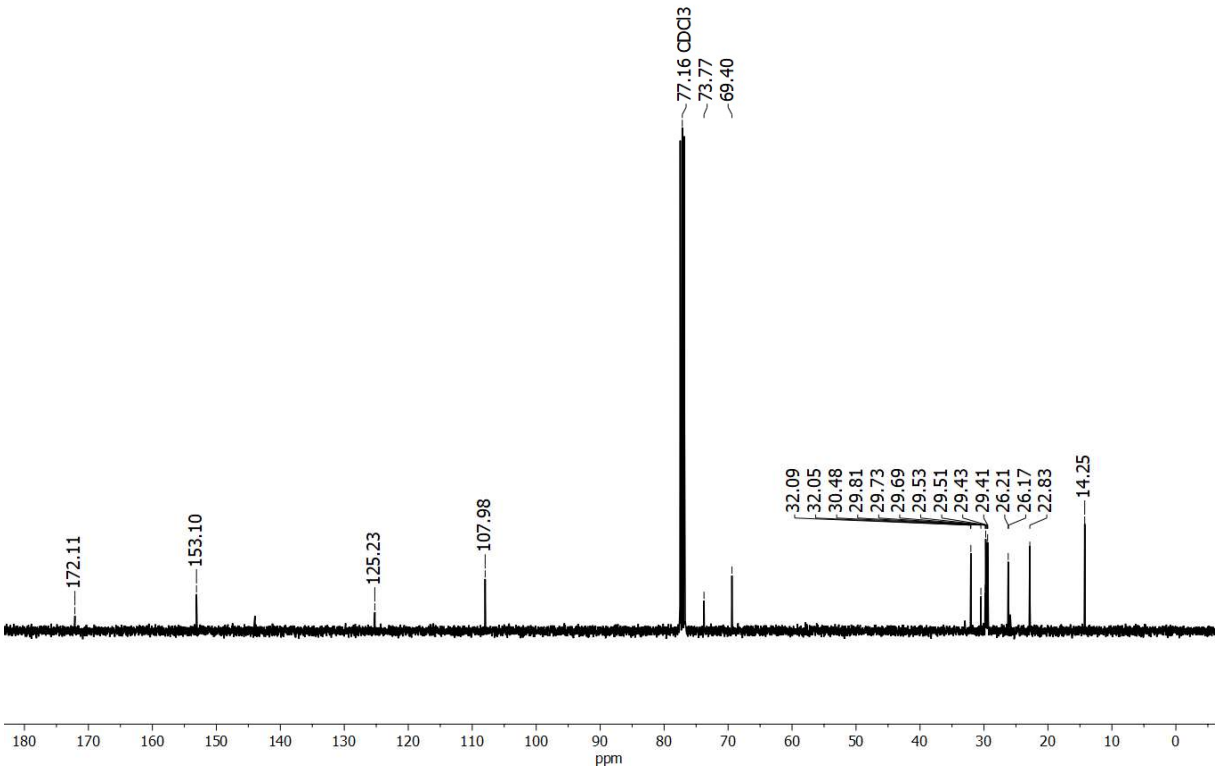


Figure S106. ^{13}C-NMR spectra of compound **34d** dissolved in $CDCl_3$.

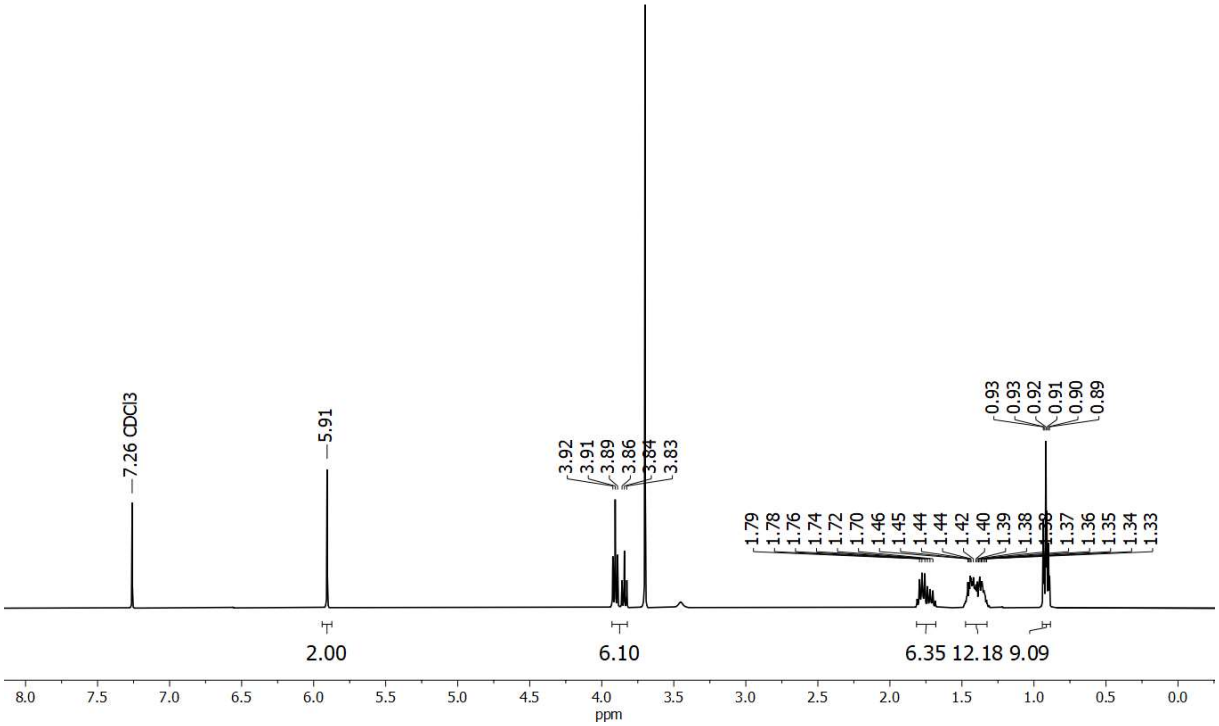


Figure S107. ^{1}H-NMR spectra of compound **36b** dissolved in $CDCl_3$.

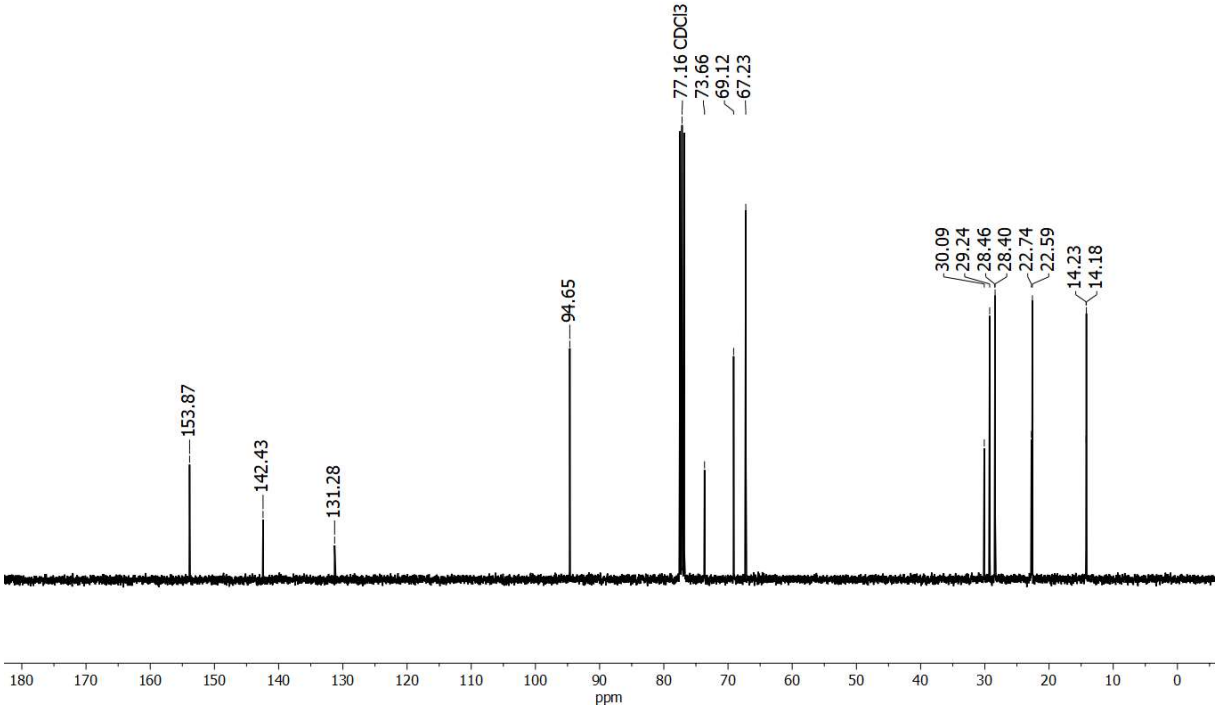


Figure S108. ^{13}C-NMR spectra of compound **36b** dissolved in $CDCl_3$.

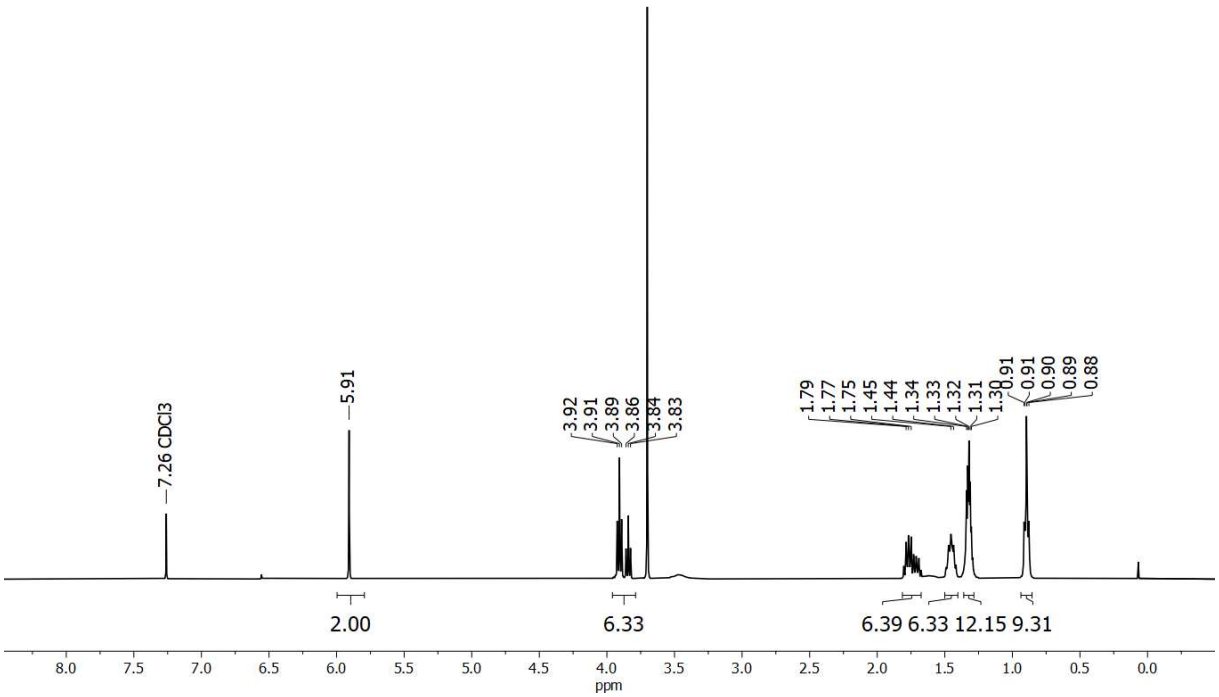


Figure S109. ^{1}H-NMR spectra of compound **36c** dissolved in $CDCl_3$.

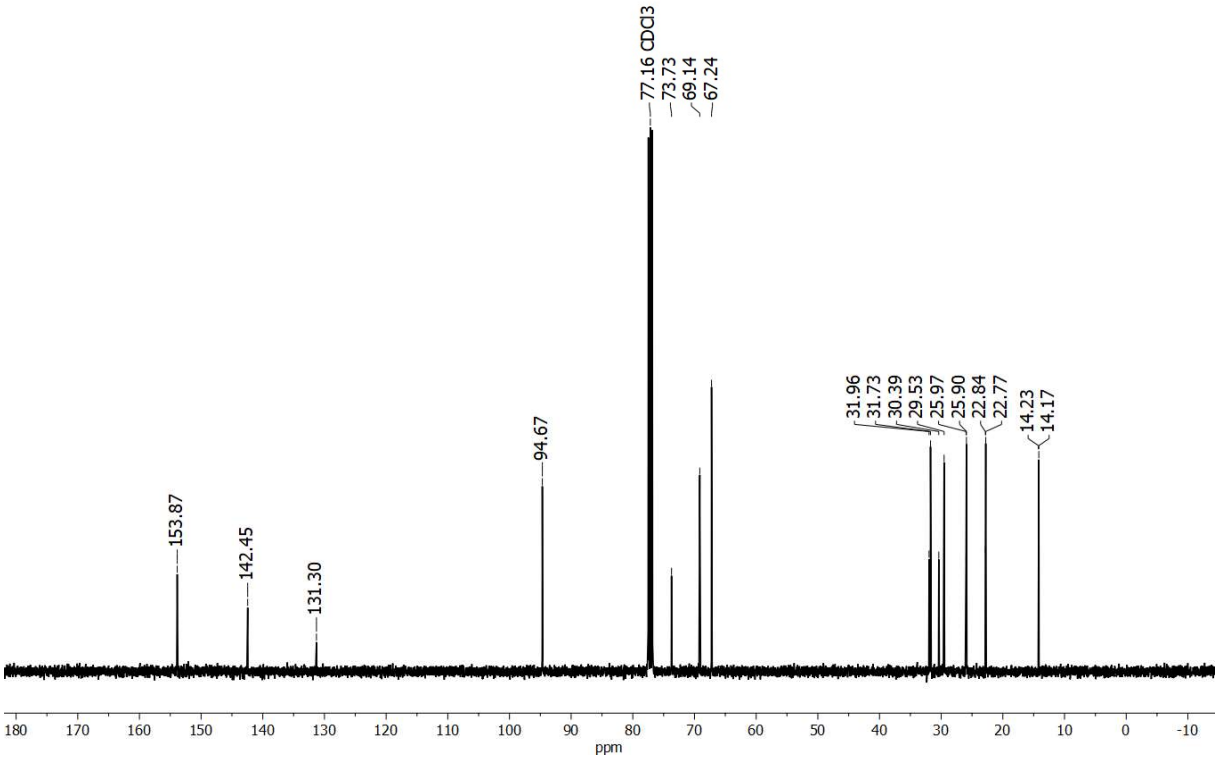


Figure S110. ^{13}C-NMR spectra of compound **36c** dissolved in $CDCl_3$.

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[3] A. Das, S. Ghosh, *Chem. Commun.* **2011**, *47*, 8922.