

# Synthesis, electrochemical and photophysical properties of calixarene based Ru(II) complexes as potential multivalent photoreagents

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## Supporting Information

Syntheses of the intermediate compounds **5**, **11**, **12**, **17**, **18** and **23**.

**Figure S1.** <sup>1</sup>H NMR spectrum (300 MHz, 298K) of compound **5** in CDCl<sub>3</sub>.

**Figure S2.** <sup>13</sup>C NMR spectrum (75 MHz, 298K) of compound **5** in CDCl<sub>3</sub>.

**Figure S3.** COSY NMR spectrum (300MHz, 298K) of compound **5** in CDCl<sub>3</sub>.

**Figure S4.** HSQC NMR spectrum (300MHz, 298K) of compound **5** in CDCl<sub>3</sub>.

**Figure S5.** <sup>1</sup>H NMR spectrum (300 MHz, 298K) of compound **6** in CDCl<sub>3</sub>.

**Figure S6.** <sup>13</sup>C NMR spectrum (75 MHz, 298K) of compound **6** in CDCl<sub>3</sub>.

**Figure S7.** COSY NMR spectrum (300MHz, 298K) of compound **6** in CDCl<sub>3</sub>.

**Figure S8.** HSQC NMR spectrum (300MHz, 298K) of compound **6** in CDCl<sub>3</sub>.

**Figure S9.** <sup>1</sup>H NMR spectrum (300 MHz, 298K) of compound **7** in CD<sub>3</sub>OD.

**Figure S10.** <sup>13</sup>C NMR spectrum (75 MHz, 298K) of compound **7** in CD<sub>3</sub>OD.

**Figure S11.** COSY NMR spectrum (300MHz, 298K) of compound **7** in CD<sub>3</sub>OD.

**Figure S12.** HSQC NMR spectrum (300MHz, 298K) of compound **7** in CD<sub>3</sub>OD.

**Figure S13.** <sup>1</sup>H NMR spectrum (300 MHz, 298K) of compound **11** in CDCl<sub>3</sub>.

**Figure S14.** <sup>1</sup>H NMR spectrum (600 MHz, 298K) of compound **12** in CDCl<sub>3</sub>.

**Figure S15.** <sup>13</sup>C NMR spectrum (75 MHz, 298K) of compound **12** in CDCl<sub>3</sub>.

**Figure S16.** COSY NMR spectrum (300MHz, 298K) of compound **12** in CDCl<sub>3</sub>.

**Figure S17.** HSQC NMR spectrum (300MHz, 298K) of compound **12** in CDCl<sub>3</sub>.

**Figure S18.** HMBC NMR spectrum (600MHz, 298K) of compound **12** in CDCl<sub>3</sub>.

**Figure S19.** <sup>1</sup>H NMR spectrum (300 MHz, 298K) of compound **13** in CDCl<sub>3</sub>.

**Figure S20.** <sup>13</sup>C NMR spectrum (75 MHz, 298K) of compound **13** in CDCl<sub>3</sub>.

**Figure S21.** COSY NMR spectrum (300MHz, 298K) of compound **13** in CDCl<sub>3</sub>.

**Figure S22.** HSQC NMR spectrum (300MHz, 298K) of compound **13** in CDCl<sub>3</sub>.

**Figure S23.** HMBC NMR spectrum (400MHz, 298K) of compound **13** in CDCl<sub>3</sub>.

**Figure S24.** <sup>1</sup>H NMR spectrum (300 MHz, 298K) of compound **14** in CDCl<sub>3</sub>.

**Figure S25.** <sup>13</sup>C NMR spectrum (100 MHz, 298K) of compound **14** in CDCl<sub>3</sub>.

**Figure S26.** COSY NMR spectrum (400MHz, 298K) of compound **14** in CDCl<sub>3</sub>.

**Figure S27.** HSQC NMR spectrum (400MHz, 298K) of compound **14** in CDCl<sub>3</sub>.

**Figure S28.** HMBC NMR spectrum (400MHz, 298K) of compound **14** in CDCl<sub>3</sub>.

**Figure S29.** <sup>1</sup>H NMR spectrum (300 MHz, 298K) of compound **17** in CDCl<sub>3</sub>.

**Figure S30.** <sup>13</sup>C NMR spectrum (75 MHz, 298K) of compound **17** in CDCl<sub>3</sub>.

**Figure S31.** COSY NMR spectrum (300MHz, 298K) of compound **17** in CDCl<sub>3</sub>.

**Figure S32.** HSQC NMR spectrum (300MHz, 298K) of compound **17** in CDCl<sub>3</sub>.

**Figure S33.** <sup>1</sup>H NMR spectrum (400 MHz, 298K) of compound **18** in CDCl<sub>3</sub>.

**Figure S34.** <sup>13</sup>C NMR spectrum (75 MHz, 298K) of compound **18** in CDCl<sub>3</sub>.

**Figure S35.** COSY NMR spectrum (400MHz, 298K) of compound **18** in CDCl<sub>3</sub>.

**Figure S36.** HSQC NMR spectrum (400MHz, 298K) of compound **18** in CDCl<sub>3</sub>.

**Figure S37.** HMBC NMR spectrum (400MHz, 298K) of compound **18** in CDCl<sub>3</sub>.

**Figure S38.**  $^1\text{H}$  NMR spectrum (400 MHz, 328K) of compound **19** in  $\text{CDCl}_3$ .

**Figure S39.**  $^{13}\text{C}$  NMR spectrum (100 MHz, 298K) of compound **19** in  $\text{CDCl}_3$ .

**Figure S40.** COSY NMR spectrum (400MHz, 298K) of compound **19** in  $\text{CDCl}_3$ .

**Figure S41.** HSQC NMR spectrum (400MHz, 298K) of compound **19** in  $\text{CDCl}_3$ .

**Figure S42.** HMBC NMR spectrum (400MHz, 298K) of compound **19** in  $\text{CDCl}_3$ .

**Figure S43.**  $^1\text{H}$  NMR spectrum (300 MHz, 298K) of compound **23** in  $\text{CDCl}_3$ .

**Figure S44.**  $^{13}\text{C}$  NMR spectrum (75 MHz, 298K) of compound **23** in  $\text{CDCl}_3$ .

**Figure S45.** COSY NMR spectrum (300MHz, 298K) of compound **23** in  $\text{CDCl}_3$ .

**Figure S46.** HSQC NMR spectrum (300MHz, 298K) of compound **23** in  $\text{CDCl}_3$ .

**Figure S47.** HMBC NMR spectrum (400MHz, 298K) of compound **23** in  $\text{CDCl}_3$ .

**Figure S48.**  $^1\text{H}$  NMR spectrum (400 MHz, 298K) of compound **24** in  $\text{CD}_3\text{OD}$ .

**Figure S49.**  $^{13}\text{C}$  NMR spectrum (75 MHz, 298K) of compound **24** in  $\text{CD}_3\text{OD}$ .

**Figure S50.** COSY NMR spectrum (300MHz, 298K) of compound **24** in  $\text{CD}_3\text{OD}$ .

**Figure S51.** HSQC NMR spectrum (300MHz, 298K) of compound **24** in  $\text{CD}_3\text{OD}$ .

**Figure S52.** HMBC NMR spectrum (400MHz, 298K) of compound **24** in  $\text{CD}_3\text{OD}$ .

**Figure S53.** Cyclic voltammetry: Reduction waves of  $[\text{Ru}(\text{TAP})_2\text{pytz}'(\text{diN}_3\text{C6})]^{2+}(\text{NO}_3^-)_2$  **24**.

**Figure S54.** Absorption spectra (298K, air) in MeCN for complexes **6** (black), **7** (red), **13** (blue), **14** (green), **19** (orange) and **24** (pink).

**Figure S55.** Stern-Volmer experiment for  $[\text{Ru}(\text{TAP})_2\text{phen}]^{2+}$  **25** in acetonitrile, in presence of phenol.

**Figure S56.** Stern-Volmer experiment for  $[\text{Ru}(\text{TAP})_2\text{phen}]^{2+}$  **25** in acetonitrile, in presence of an acid (paratoluene sulfonic acid = PTSA).

**Figure S57.** Deuteration of the phenol moiety was checked by  $^1\text{H}$  NMR (300 MHz, 298K) in  $\text{CDCl}_3$ .

**Figure S58.** Stern-Volmer experiment for  $[\text{Ru}(\text{TAP})_2\text{phen}]^{2+}$  **25** in acetonitrile, in presence of deuterated phenol.

**Figure S59.** Equation for  $\Delta G_{PCET}^0$  in the case of a PCET: (1.2) ET followed by HT or (1.3) ET and HT concerted.

**Instrumentation.** The  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and 2D NMR spectra were recorded with a Bruker Avance-300 instrument, a Varian-400 VNMRJ System and a Bruker Varian Unity-600. The chemical shifts are expressed in ppm and determined in comparison of the deuterated solvent used as internal reference ( $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$ ).  $\text{CDCl}_3$  was filtered over a short basic alumina column to remove traces of  $\text{DCl}$ . Most of the  $^1\text{H}$  NMR spectra signals were attributed through 2D NMR analyses (COSY, HSQC, HMBC). The electrospray mass spectra were recorded with a Q-TOF 6520 Agilent Technology spectrometer (at the Organic Pharmaceutical Chemistry Lab). ATR-FTIR spectra were recorded, at room temperature, on a Bruker IFS55 FTIR spectrophotometer equipped with a liquid nitrogen-cooled mercurycadmium-telluride (MCT) detector at a nominal resolution of  $2\text{ cm}^{-1}$  and encoded every  $1\text{ cm}^{-1}$ . The emission spectra were recorded with a Shimadzu RF-5301PC and the absorption spectra with a Perkin-Elmer Lambda UV-Vis spectrophotometer. The determination of the molar absorption coefficients were performed by weight and absorption measurements. Cyclic voltammetry was carried out on a platinum disk working electrode (approximate area =  $3\text{mm}^2$ ), in dried acetonitrile with tetrabutylammonium hexafluorophosphate ( $0.1\text{ mol.L}^{-1}$ ) as supporting electrolyte. The potential of the working electrode was controlled by an Autolab PGSTAT 100 (Eco Chemie B.V., Utrecht, The Netherlands) potentiostat through a PC interface with a scan rate of  $100\text{ mV s}^{-1}$  between  $-2$  and  $+2\text{ V}$  versus SCE. The counter electrode was a platinum disk and the reference electrode a Saturated Calomel Electrode (SCE). All measurements were performed in a single compartment cell. The emission lifetimes were measured by using the single-photon counting technique (SPC) with an Edinburgh Instruments FL900 spectrometer (Edinburgh, U.K.) equipped with a nitrogen-filled discharge lamp and a peltier-cooled Hamamatsu R955s photomultiplier tube. The emission

decays were analyzed with the Edinburgh Instruments software (version 3.0), based on nonlinear least-squares regressions using Marquardt algorithms.

The transients induced under pulsed illumination were measured by using as excitation a source composed of a frequency-tripled (355 nm) Nd:YAG Q-switched laser (Continuum Inc.) coupled with an optical parametric oscillator (Continuum Inc.) covering the wavelengths region 410-2300 nm with a maximum pulse energy from 10 to 120 mJ depending on the wavelength. The emission was detected perpendicularly by a photomultiplier (R928, Hamamatsu). The signal was recorded with a digital oscilloscope (HP 54200A), connected through the IEEE488 interface to a personal computer, and was averaged over at least 16 shots. The emission wavelength was selected via a grating Czerny-Turner monochromator (Spectra Pro 2300i, Acton Research Corp.). For the transient absorption, a cross-beam configuration was adapted by using as a probe source a 150 W xenon arc lamp producing a continuous spectral distribution ranging from 190 to 2600 nm. Complete transient absorption spectra were measured in the 200-650 nm spectral range with a 2 ns gated intensified CCD camera (PIMAX, 1024 x 256 pixels, Princeton Instruments). The time delays for probing, following the laser excitation pulse, were controlled by a programmable time generator (Princeton Instruments). For kinetic analyses, the transient absorption traces at selected individual wavelengths were recorded by the photomultiplier as emission lifetime measurement. Kinetic analyses of the absorption traces were performed by nonlinear least-squares regression modified by Levenberg-Marquardt algorithms.<sup>1</sup>

**Synthesis of calix[4]monoamidophenanthroline 5.** Calix[4]monoacide **4** (0.296 g, 0.419 mmol, 1 equiv.), DCC (0.131 g, 0.636 mmol, 1.5 equiv.) and HOBt (0.087 g, 0.644 mmol, 1.5 equiv.) were dissolved in DMF (7 mL). At 0°C, DIPEA (450  $\mu$ L, 2.59 mmol, 6.2 equiv.) was added to the mixture which was stirred for 30 min at 0°C under inert atmosphere. Then, 5-

glycinamido-1,10-phenanthroline **22** (0.296 g, 0.809 mmol, 2 equiv.) was added to the mixture which was stirred for 16h at room temperature under inert atmosphere. The reaction mixture was concentrated under reduced pressure and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (60 mL). The organic layer was washed with H<sub>2</sub>O (3×35 mL) and the combined aqueous layers were extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×45 mL). The combined organic layers were concentrated under reduced pressure. Ether (3 mL) was added and DCU was filtered. The filtrate was concentrated under reduced pressure and the crude residue was purified by flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9:1) to yield the compound **5** as a clear yellow solid (0.352 g, 0.329 mmol, 78%). R<sub>f</sub> = 0.42 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9:1).

m.p. 182-184°C (dec.); IR:  $\nu$ : 3319, 2966, 1683, 1485, 1298 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298K):  $\delta_{\text{(ppm)}}$  = 1.17 (s, 9H, *t*Bu), 1.22 (s, 18H, *t*Bu), 1.23 (s, 9H, *t*Bu), 3.46 (d, <sup>2</sup>J = 14.1 Hz, 2H, ArCH<sub>2eq</sub>), 3.51 (d, <sup>2</sup>J = 13.5 Hz, 2H, ArCH<sub>2eq</sub>), 4.21 (d, <sup>2</sup>J = 13.8 Hz, 2H, ArCH<sub>2ax</sub>), 4.25 (d, <sup>2</sup>J = 13.5 Hz, 2H, ArCH<sub>2ax</sub>), 4.52 (d, <sup>3</sup>J = 5.4 Hz, 2H, NCH<sub>2</sub>), 4.77 (s, 2H, OCH<sub>2</sub>), 7.02 (d, <sup>4</sup>J = 2.4 Hz, 2H, ArH), 7.07-7.09 (m, 6H, ArH), 7.56 (dd, 1H, <sup>3</sup>J = 4.5 Hz, <sup>3</sup>J = 8.4 Hz, H<sub>3</sub>), 7.66 (dd, <sup>3</sup>J = 4.5 Hz, <sup>3</sup>J = 8.1 Hz, 1H, H<sub>8</sub>), 8.25 (dd, <sup>4</sup>J = 1.2 Hz, <sup>3</sup>J = 8.3 Hz, 1H, H<sub>7</sub>), 8.43 (s, 1H, H<sub>6</sub>), 8.62 (d, <sup>3</sup>J = 8.7 Hz, 1H, H<sub>4</sub>), 9.05 (d, <sup>3</sup>J = 4.2 Hz, 1H, H<sub>2</sub>), 9.14 (d, <sup>4</sup>J = 1.2 Hz, <sup>3</sup>J = 4.5 Hz, 1H, H<sub>9</sub>), 9.49 (s<sub>b</sub>, 2H, OH), 10.06 (s<sub>b</sub>, 1H, OH), 10.06-10.22 (s<sub>b</sub>, 2H, NH<sub>phen</sub> + NH<sub>amide</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 298K):  $\delta_{\text{(ppm)}}$  = 31.2, 31.5(7), 31.6(2), 32.4, 33.1, 34.1, 34.2, 34.5, 45.5, 75.3, 118.1, 123.6, 123.9, 126.1, 126.4, 127.2, 127.4, 127.8, 128.2, 128.8, 131.4, 131.6, 132.9 (2C), 137.5, 144.3, 144.4, 145.6, 146.9, 147.0, 148.0, 148.9, 149.0, 149.7, 149.9, 170.0, 168.7, 170.6; HRMS (ESI-TOF) calcd for C<sub>60</sub>H<sub>68</sub>N<sub>4</sub>O<sub>6</sub> (M+H)<sup>+</sup> 941.5217, found 941.5196.

**Synthesis of calix[6]monoacid 11.** Calix[6]monoamide **10** (0.628 g, 0.586 mmol, 1 equiv.) was dissolved in dioxane (30 mL). An aqueous HCl solution (6 M, 3 mL) was added dropwise and the mixture was stirred for 4 days at 56°C under inert atmosphere. The reaction mixture was

concentrated under reduced pressure and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The organic layer was washed with H<sub>2</sub>O (4×50 mL) until pH = 5-6 and concentrated under reduced pressure to yield the compound **11** as a white solid (0.629 g, 0.586 mmol, quant.).

m.p. 171-172°C (dec.); IR:  $\nu$ : 2956, 1684, 1484 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298K):  $\delta_{\text{(ppm)}}$  = 0.98 (s, 18H, *t*Bu), 1.06 (s, 18H, *t*Bu), 1.17 (s, 9H, *t*Bu), 1.38 (s, 9H, *t*Bu), 2.87 (s, 2H, OCH<sub>2</sub>), 3.77-3.84 (m, 7H, OMe + ArCH<sub>2</sub>), 3.84-3.94 (m, 10H, OMe + ArCH<sub>2</sub>), 3.95-4.07 (m, 4H, ArCH<sub>2</sub>), 6.69 (d, 2H, <sup>4</sup>J = 2.2 Hz, ArH), 6.75 (d, 2H, <sup>4</sup>J = 2.3 Hz, ArH), 6.96-6.98 (m, 4H, ArH), 7.01 (s, 2H, ArH), 7.24-7.28 (m, 2H, ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 293K):  $\delta_{\text{(ppm)}}$  = 169.8, 153.6, 152.9, 151.9, 149.3, 147.2, 146.6, 142.4, 133.5, 133.3, 132.8, 127.8, 127.5, 126.6, 126.4, 125.6, 125.3, 125.0, 124.8, 68.9, 61.8, 61.7, 34.5, 34.4, 34.3, 33.9, 31.9, 31.8, 31.6, 31.3, 30.1; HRMS (ESI-TOF) calcd for C<sub>71</sub>H<sub>92</sub>O<sub>8</sub> (M+H)<sup>+</sup> 1073.6870, found 1073.6931.

**Synthesis of calix[6]monoamidephenanthroline 12.** Calix[6]monoacid **11** (0.326 g, 0.304 mmol, 1 equiv.), DCC (0.094 g, 0.456 mmol, 1.5 equiv.) and HOBt (0.062 g, 0.459 mmol, 1.5 equiv.) were dissolved in DMF (7 mL). At 0°C, DIPEA (320  $\mu$ L, 1.84 mmol, 6 equiv.) was added to the mixture which was stirred for 20min at 0°C under inert atmosphere. Then, 5-glycinamido-1,10-phenanthroline **20** was added to the mixture which was stirred for 16h at room temperature under inert atmosphere. The reaction mixture was concentrated under reduced pressure and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (60 mL). The organic layer was washed with H<sub>2</sub>O (3×35 mL) and the combined aqueous layers were extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×45 mL). The combined organic layers were concentrated under reduced pressure. Ether (3 mL) was added and DCU was filtered. The filtrate was concentrated under reduced pressure and the crude residue was purified by flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 95:5) to yield the compound **12** as a clear yellow solid (0.343 g, 0.263 mmol, 86%). R<sub>f</sub> = 0.38 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 95:5).

m.p. 185 (dec.); IR:  $\nu$ : 3310, 2965, 1687, 1483, 1210  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 298K):  $\delta_{(\text{ppm})}$  = 0.90 (s, 18H, *t*Bu), 1.16 (s, 9H, *t*Bu), 1.23 (s, 18H, *t*Bu), 1.32 (s, 9H, *t*Bu), 3.09 (s, 3H, OMe), 3.33 (s, 6H, OMe), 3.41 (d,  $^2\text{J} = 17.0$  Hz, 2H,  $\text{ArCH}_{2\text{eq}}$ ), 3.49 (d,  $^2\text{J} = 17.0$  Hz, 2H,  $\text{ArCH}_{2\text{eq}}$ ), 3.50 (d,  $^2\text{J} = 17.0$  Hz, 2H,  $\text{ArCH}_{2\text{eq}}$ ), 4.05-4.09 (m, 4H,  $\text{ArCH}_{2\text{ax}}$ ), 4.17 (s, 2H,  $\text{OCH}_2$ ), 4.33 (d,  $^3\text{J} = 4.8$  Hz, 2H,  $\text{NCH}_2$ ), 4.47 (d,  $^2\text{J} = 17.0$  Hz, 2H,  $\text{ArCH}_{2\text{ax}}$ ), 6.72 (s, 2H, ArH), 6.85 (s, 2H, ArH), 6.96 (d,  $^4\text{J} = 2.4$  Hz, 2H, ArH), 7.02 (d,  $^4\text{J} = 1.8$  Hz, 2H, ArH), 7.03 (s, 2H, ArH), 7.25 (s, 2H, ArH), 7.34 (sb, 2H, OH), 7.36 (dd,  $^3\text{J} = 4.2$  Hz,  $^3\text{J} = 8.4$  Hz, 1H,  $\text{H}_3$ ), 7.47 (dd,  $^3\text{J} = 4.2$  Hz,  $^3\text{J} = 8.4$  Hz, 1H,  $\text{H}_8$ ), 7.77 (sb, 1H,  $\text{NH}_{\text{amide}}$ ), 7.81 (d,  $^3\text{J} = 7.8$  Hz, 1H,  $\text{H}_7$ ), 7.93 (s, 1H,  $\text{H}_6$ ), 8.43 (d,  $^3\text{J} = 7.8$  Hz, 1H,  $\text{H}_4$ ), 9.05-9.07 (m, 2H,  $\text{H}_{2,9}$ ), 9.22 (sb, 1H,  $\text{NH}_{\text{phen}}$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298K):  $\delta_{(\text{ppm})}$  = 30.5, 31.1 (2C), 31.2, 31.4, 31.6, 31.7, 34.0, 34.2, 34.3(6), 34.4(3), 45.0, 61.5, 61.7, 71.5, 120.8, 123.2 (2C), 124.7, 125.4, 126.0, 126.1, 126.3, 126.6, 127.3, 128.3, 131.0, 131.1, 132.4, 132.7, 132.9, 133.2, 136.0, 142.5 (2C), 144.8, 146.5, 146.7 (2C), 147.5, 147.6, 149.8, 170.1, 170.2, 171.7, 171.9, 172.7, 169.5, 171.5; HRMS (ESI-TOF) calcd for  $\text{C}_{85}\text{H}_{102}\text{N}_4\text{O}_8$  ( $\text{M}+\text{H}$ ) $^+$  1307.7776, found 1307.7762.

**Synthesis of calix[6]monoazido 17.**  $\text{NaN}_3$  (0.285 g, 4.38 mmol, 4.9 equiv.) was suspended in  $\text{CH}_3\text{CN}$  (16 mL). Trifluoromethanesulfonic anhydride ( $\text{Tf}_2\text{O}$ ) (0.510 mL, 3.07 mmol, 3.4 equiv.) was added drop by drop at  $0^\circ\text{C}$ . The mixture was stirred for 2h at  $0^\circ\text{C}$  under inert atmosphere. Calix[6]monoamine **16** (1.049 g, 0.896 mmol, 1 equiv.) was dissolved in toluene (16 mL). Triethylamine (0.790 mL, 5.63 mmol, 6.3 equiv.) and  $\text{CuSO}_4$  (0.013 g, 0.0815 mmol, 0.09 equiv.) were added. At  $0^\circ\text{C}$ , the solution containing  $\text{TfN}_3$  was added drop by drop to the reaction mixture which was stirred for 16h at room temperature under inert atmosphere. An aqueous  $\text{NH}_4\text{OH}$  solution (25%, 15 mL) was added to the mixture which was stirred for 40min and the aqueous layer was washed with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10\text{mL}$ ). The combined organic layers were

concentrated under reduced pressure and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The organic layer was washed with an aqueous HCl solution (10%, 15 mL) and the mixture was stirred for 45 min at room temperature. Then, the organic layer was washed with H<sub>2</sub>O (3×15 mL) until pH = 7 and concentrated under reduced pressure to yield the compound **17** as a clear yellow solid (0.669 g, 0.616 mmol, 69%).

m.p. 166°C; IR:  $\nu$ : 2961, 2110, 1484, 1210 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298K):  $\delta_{\text{(ppm)}}$  = 0.60 (s, 9H, *t*Bu), 1.02 (s, 18H, *t*Bu), 1.26 (s, 18H, *t*Bu), 1.39 (s, 9H, *t*Bu), 2.12 (t<sub>b</sub>, <sup>3</sup>J = 4.5 Hz, 2H, CH<sub>2</sub>N<sub>3</sub>), 2.67 (t<sub>b</sub>, <sup>3</sup>J = 4.5 Hz, 2H, OCH<sub>2</sub>), 3.52 (s, 3H, OMe), 3.85-3.95 (m, 14H, ArCH<sub>2</sub> + OMe), 4.01-4.11 (m, 4H, ArCH<sub>2</sub>), 6.22 (s<sub>b</sub>, 2H, ArH), 6.85 (d, <sup>4</sup>J = 2.4 Hz, 2H, ArH), 6.97 (d, 2H, <sup>4</sup>J = 2.2 Hz, ArH), 7.02 (d, <sup>4</sup>J = 2.4 Hz, 2H, ArH), 7.18 (d, <sup>4</sup>J = 2.4 Hz, 2H, ArH), 7.23 (s, 2H, ArH), 7.28 (s, 2H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 298K):  $\delta_{\text{(ppm)}}$  = 29.7, 30.9, 31.2(6), 31.3(4), 31.6(8), 31.7(4), 32.1, 33.8, 34.0, 34.3, 50.0, 60.4, 61.7, 72.3, 124.4, 125.0, 125.6, 126.3, 126.5, 126.7, 127.1, 128.1, 132.1(7), 132.2(2), 133.1, 133.3, 142.3, 145.5, 146.1, 147.3, 150.6, 151.4, 153.3, 153.8; HRMS (ESI-TOF) calcd for C<sub>71</sub>H<sub>93</sub>N<sub>3</sub>O<sub>6</sub> (M+H)<sup>+</sup> 1084.7143, found 1084.7109.

**Caution!** Although we have not encountered any problem, it is noted that small azide derivatives are potentially explosive and should be handled with appropriate precautions.<sup>32</sup>

**Synthesis of calix[6]monopytz 18.** Calix[6]monoazido **17** (0.403 g, 0.371 mmol, 1 equiv.) and 2-(trimethylsilyl)ethynylpyridine (0.124 g, 0.709 mmol, 2 equiv.) were dissolved in a mixture of *t*-BuOH/H<sub>2</sub>O (1:1) (7 mL) and in CH<sub>2</sub>Cl<sub>2</sub> (7 mL). CuSO<sub>4</sub> (0.077 g, 0.484 mmol, 1.3 equiv.), sodium ascorbate (0.116 g, 0.586 mmol, 1.6 equiv.) and K<sub>2</sub>CO<sub>3</sub> (0.057 g, 0.413 mmol, 1.1 equiv.) were successively added and the mixture was stirred vigorously for 2h30 at room temperature under inert atmosphere. CH<sub>2</sub>Cl<sub>2</sub> (190 mL) and an aqueous NH<sub>4</sub>OH solution (25%,

58 mL) were added and the mixture was stirred for 2h at room temperature. The organic layer was washed with an aqueous  $\text{NH}_4\text{OH}$  solution (25%, 50 mL) and the combined aqueous layers were extracted with  $\text{CH}_2\text{Cl}_2$  (2×50 mL). The combined organic layers were washed with  $\text{H}_2\text{O}$  (4×150 mL) until pH = 7 and concentrated under reduced pressure. The crude residue was purified by flash chromatography ( $\text{CH}_2\text{Cl}_2/\text{AcOEt}$  9:1) to yield the compound **18** as a white solid (0.316 g, 0.266 mmol, 72%). Rf = 0.28 ( $\text{CH}_2\text{Cl}_2/\text{AcOEt}$  9:1).

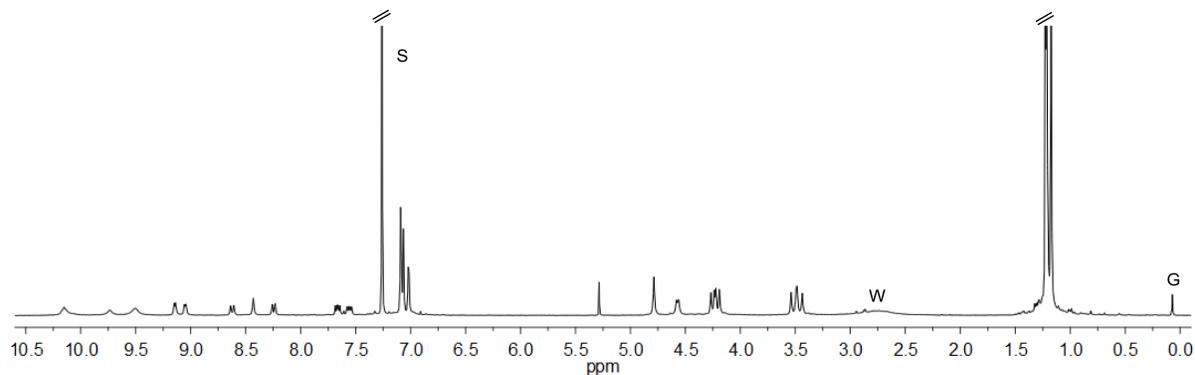
m.p. 145-147°C (dec.); IR:  $\nu$ : 3384, 2961, 1483, 1209, 1011  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298K):  $\delta_{(\text{ppm})}$  = 0.92 (s, 9H, *t*Bu), 1.02 (s, 18H, *t*Bu), 1.15 (s, 18H, *t*Bu), 1.39 (s, 9H, *t*Bu), 2.98 (s, 3H, OMe), 3.06 (*s*<sub>b</sub>, 2H, OCH<sub>2</sub>), 3.49 (d,  $^2\text{J}$  = 15.6 Hz, 2H, ArCH<sub>2</sub>*eq*), 3.53-3.60 (m, 4H, ArCH<sub>2</sub>*eq*), 3.75 (s, 6H, OMe), 3.97 (*s*<sub>b</sub>, 2H, NCH<sub>2</sub>), 4.20-4.28 (m, 4H, ArCH<sub>2</sub>*ax*), 4.41 (d,  $^2\text{J}$  = 15.6 Hz, 2H, ArCH<sub>2</sub>*ax*), 6.67 (s, 2H, ArH), 6.82-6.89 (m, 4H, ArH), 7.02 (s, 2H, ArH), 7.11 (d,  $^4\text{J}$  = 1.6 Hz, 2H, ArH), 7.22 (dd,  $^4\text{J}$  = 1.6 Hz,  $^3\text{J}$  = 6.0 Hz, 1H, H<sub>py</sub>), 7.25 (s, 2H, ArH), 7.75 (td,  $^4\text{J}$  = 1.2 Hz,  $^3\text{J}$  = 6.0 Hz, 1H, H<sub>py</sub>), 7.82 (*s*<sub>b</sub>, 2H, OH), 8.19 (d,  $^3\text{J}$  = 8.0 Hz, 1H, H<sub>py</sub>), 8.38 (*s*<sub>b</sub>, 1H, H<sub>tz</sub>), 8.64 (d,  $^3\text{J}$  = 4.8 Hz, 1H, H<sub>py</sub>);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298K):  $\delta_{(\text{ppm})}$  = 29.6, 29.8, 31.0, 31.3, 31.4, 31.6, 31.7, 31.8, 33.9, 34.1, 34.2(9), 34.3(3), 50.3, 60.4, 61.5, 70.4, 120.5, 122.5, 123.8, 124.5, 125.2, 125.4, 125.6, 126.0, 126.7, 126.9, 127.9, 132.5, 132.7, 133.1, 133.2, 137.0, 142.3, 146.2, 146.3, 146.9, 147.5, 149.1, 150.2, 150.9, 151.8, 152.8, 153.8; HRMS (ESI-TOF) calcd for  $\text{C}_{78}\text{H}_{99}\text{N}_4\text{O}_6$  (M+H)<sup>+</sup> 1188.7643, found 1188.7573.

**Synthesis of calix[6]diazidomonopytz 23.** Calix[6]monopytz **18** (0.206 g, 0.173 mmol, 1 equiv.) and NaH (60% in oil, 0.017 g, 0.425 mmol, 4.5 equiv.) were dissolved in a mixture of THF/DMF (1:1) (10 mL). The mixture was stirred for 20min at room temperature under inert atmosphere. 2-azidoethyl-4-methylbenzenesulfonate (0.201 g, 0.834 mmol, 4.8 equiv.) in THF (5 mL) was added and the reaction mixture was stirred for 16h at reflux under inert atmosphere.

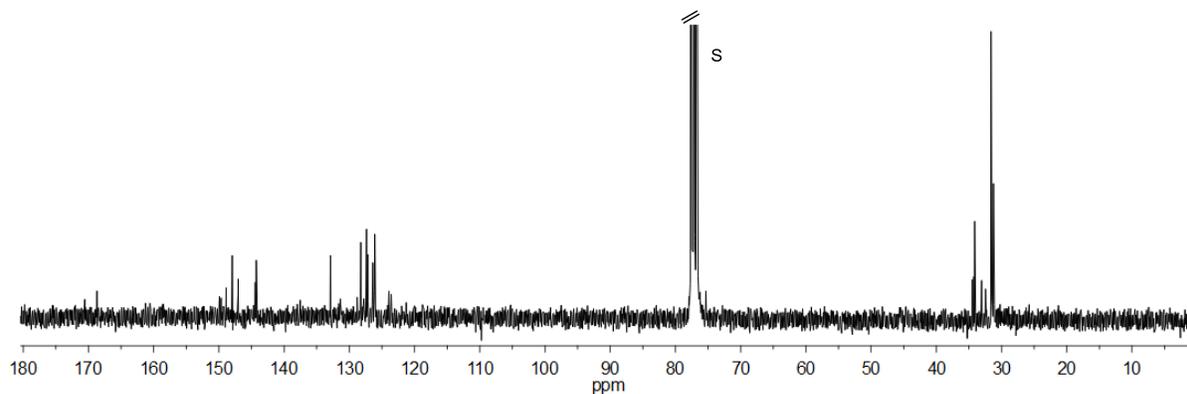
The reaction was quenched through the addition of EtOH (2 mL) and the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and the organic layer was washed with H<sub>2</sub>O (3×20 mL). The combined aqueous layers were extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and the combined organic layers were concentrated under reduced pressure. The residue was purified by flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9:1) to yield the compound **23** as a white solid (0.162 g, 0.122 mmol, 71%).

m.p. 210-212°C (dec.); IR:  $\nu$ : 3455, 2962, 2108, 1484, 1205, 1017 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298K):  $\delta_{\text{(ppm)}}$  = 0.92 (s, 27H, *t*Bu), 1.29 (s, 18H, *t*Bu), 1.32 (s, 9H, *t*Bu), 2.49 (s, 6H, OMe), 2.57 (s, 3H, OMe), 3.36 (d, <sup>2</sup>J = 15.0 Hz, 2H, ArCH<sub>2</sub>eq), 3.44-3.53 (m, 4H, CH<sub>2</sub>N<sub>3</sub>), 3.58-3.70 (m, 4H, ArCH<sub>2</sub>eq), 3.78-3.95 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>), 4.23-4.31 (m, 8H, ArCH<sub>2</sub>ax + OCH<sub>2</sub>CH<sub>2</sub>N), 4.80 (t<sub>b</sub>, <sup>3</sup>J = 5.1 Hz, 2H, CH<sub>2</sub>N), 6.74-6.82 (m, 4H, ArH), 6.80 (s, 2H, ArH), 7.14-7.17 (m, 4H, ArH), 7.18-7.22 (m, 3H, H<sub>py</sub> + ArH), 7.73 (td, <sup>4</sup>J = 1.8 Hz, <sup>3</sup>J = 7.8 Hz, 1H, H<sub>py</sub>), 8.07 (d, <sup>3</sup>J = 7.8 Hz, 1H, H<sub>py</sub>), 8.44 (s, 1H, H<sub>tz</sub>), 8.58 (d, <sup>3</sup>J = 3.9 Hz, 1H, H<sub>py</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 298K):  $\delta_{\text{(ppm)}}$  = 30.2(5), 30.3(4), 30.4, 30.5, 31.3(0), 31.3(3), 31.7 (2C), 34.2 (2C), 34.3, 34.4, 50.7, 51.2, 60.1 (2C), 70.5, 71.2, 120.5, 122.8, 123.7, 124.6, 124.7, 124.8, 127.4(8), 127.5 (2C), 133.0 (2C), 133.2, 133.4(8), 133.5(4), 133.6, 136.8, 145.9, 146.0, 146.3, 146.6, 148.5, 149.5, 150.4, 151.3, 151.7, 154.3(9), 154.4(4); HRMS (ESI-TOF) calcd for C<sub>82</sub>H<sub>104</sub>N<sub>10</sub>O<sub>6</sub> (M+H)<sup>+</sup> 1325.8219, found 1325.8192.

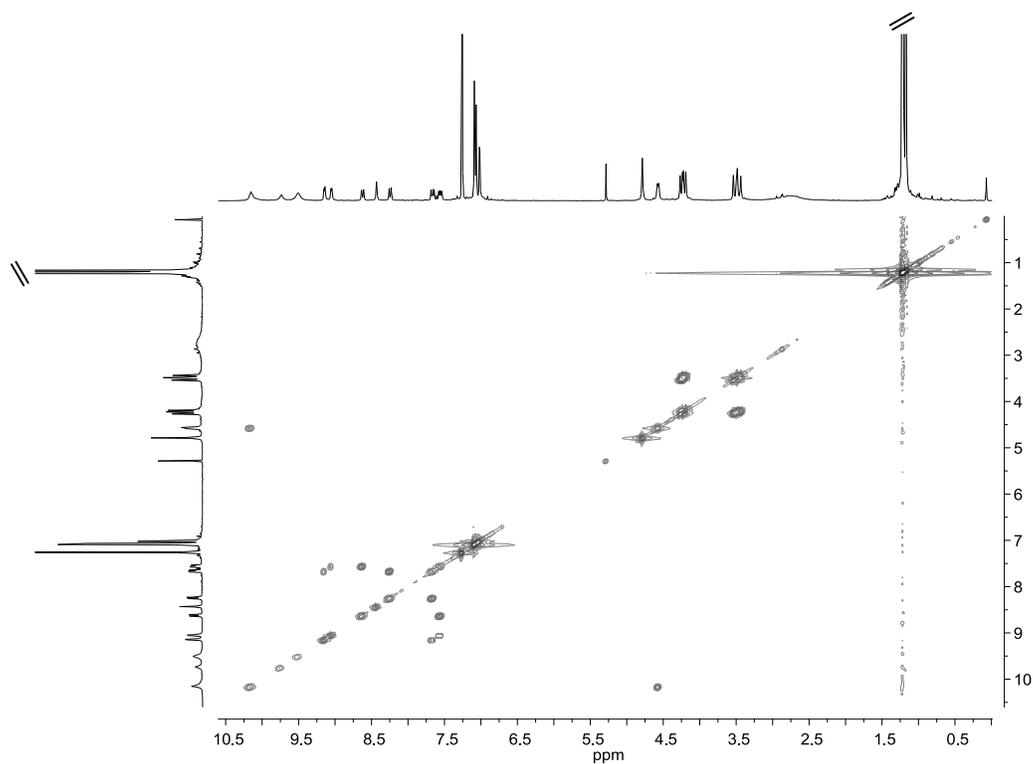
**Figure S1.**  $^1\text{H}$  NMR spectrum (300 MHz, 298K) of compound **5** in  $\text{CDCl}_3$ . S = solvent, W = water, G = grease.



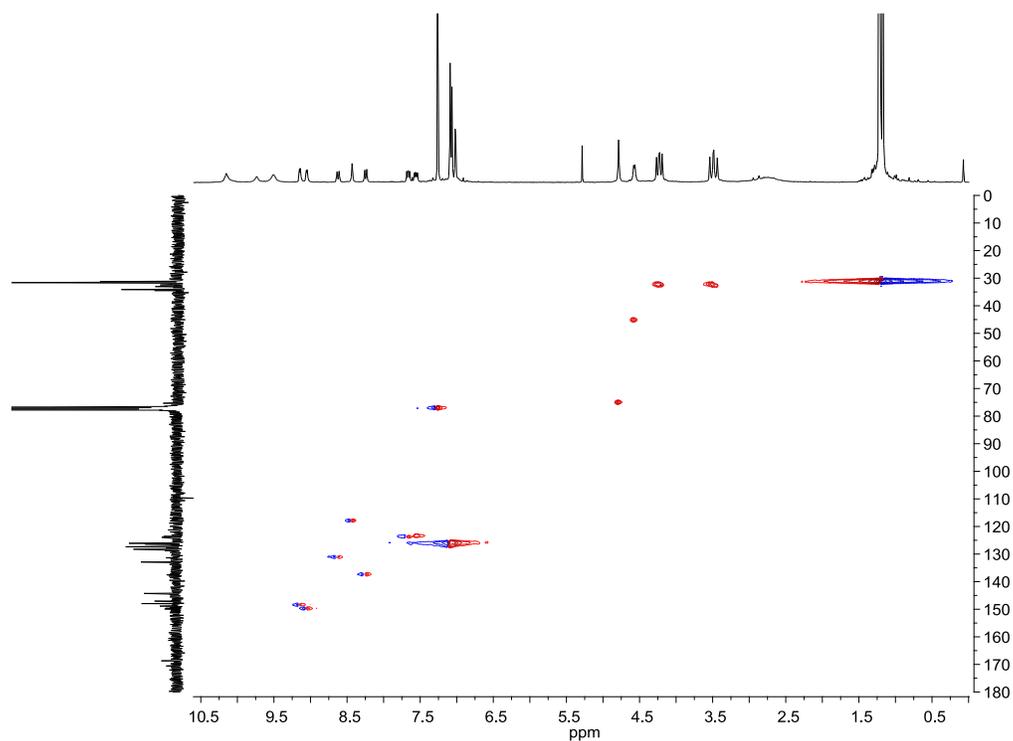
**Figure S2.**  $^{13}\text{C}$  NMR spectrum (75 MHz, 298K) of compound **5** in  $\text{CDCl}_3$ . S = solvent.



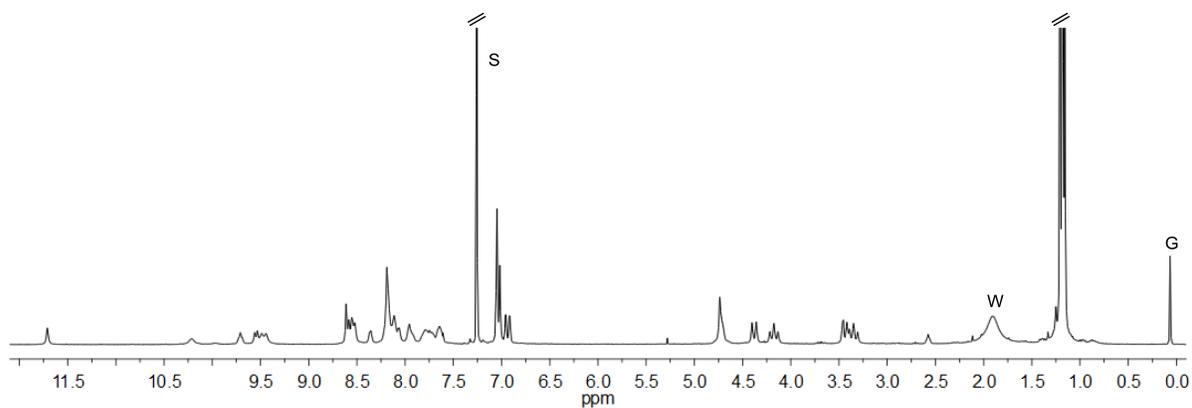
**Figure S3.** COSY NMR spectrum (300MHz, 298K) of compound **5** in CDCl<sub>3</sub>.



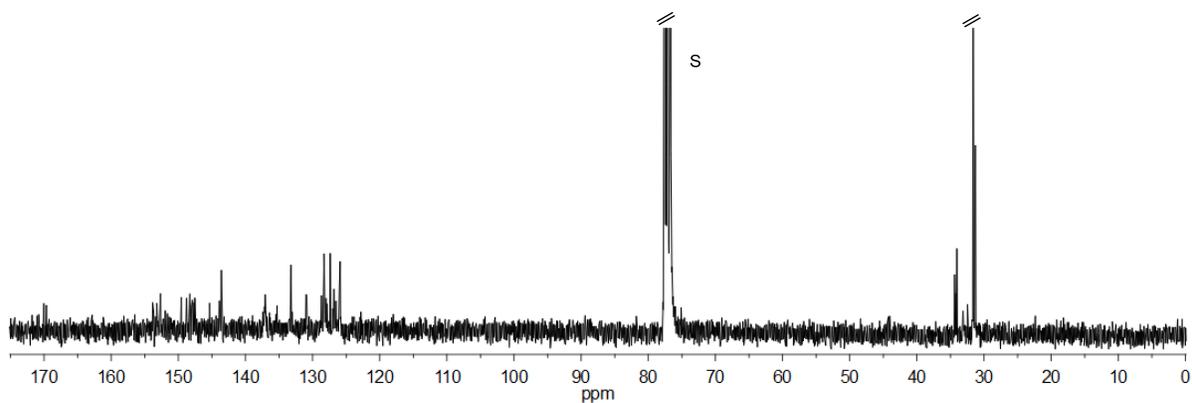
**Figure S4.** HSQC NMR spectrum (300MHz, 298K) of compound **5** in CDCl<sub>3</sub>.



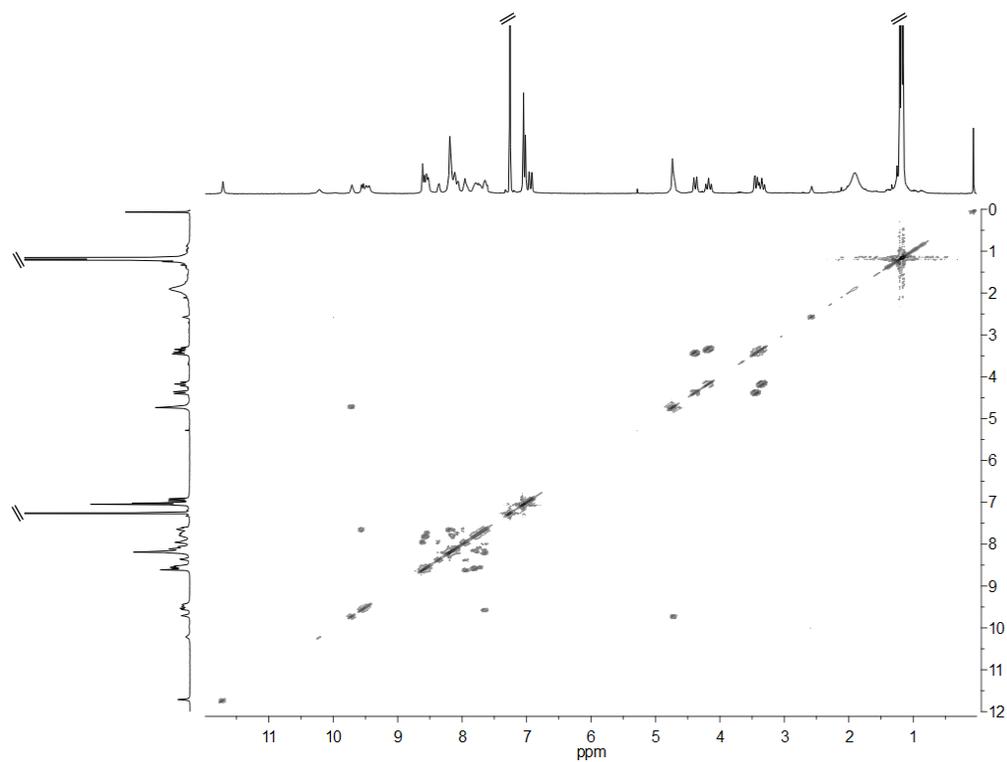
**Figure S5.**  $^1\text{H}$  NMR spectrum (300 MHz, 298K) of compound **6** in  $\text{CDCl}_3$ . S = solvent, W = water, G = grease.



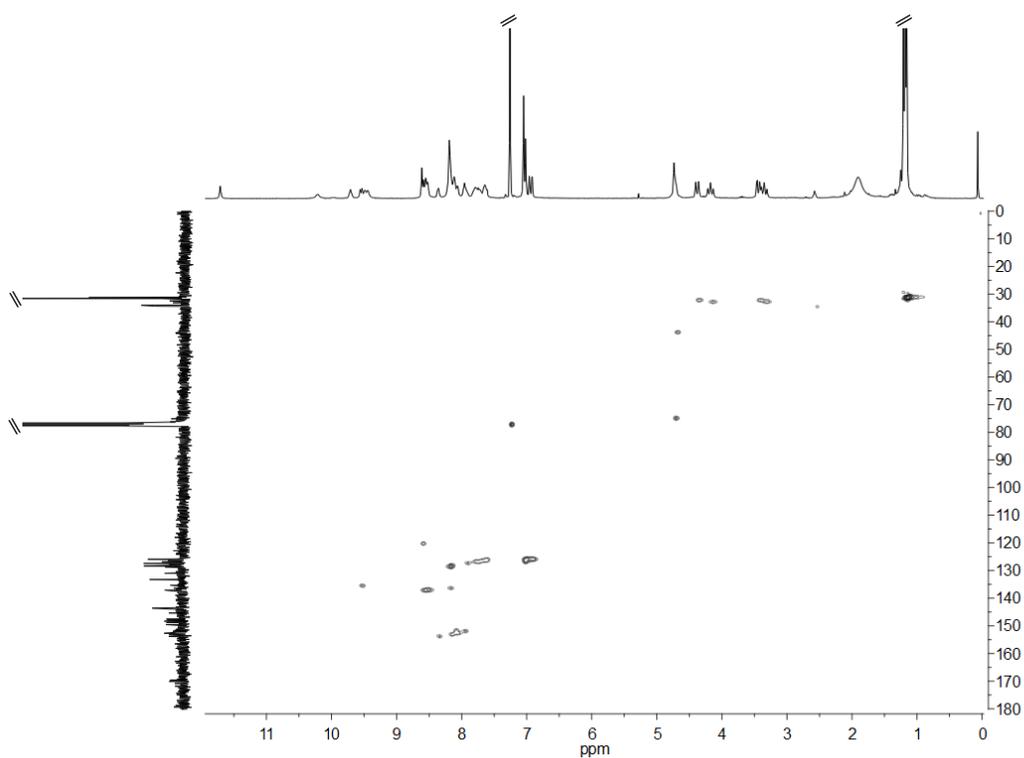
**Figure S6.**  $^{13}\text{C}$  NMR spectrum (75 MHz, 298K) of compound **6** in  $\text{CDCl}_3$ . S = solvent.



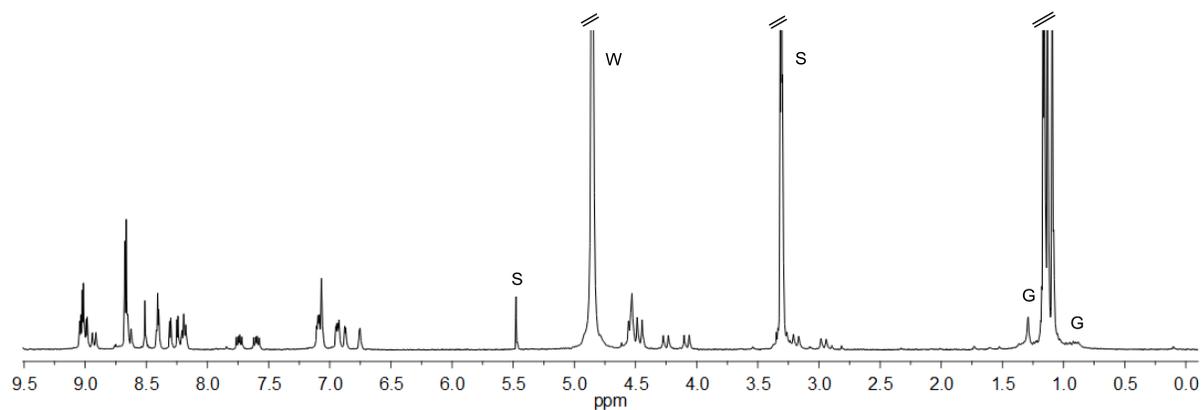
**Figure S7.** COSY NMR spectrum (300MHz, 298K) of compound **6** in  $\text{CDCl}_3$ .



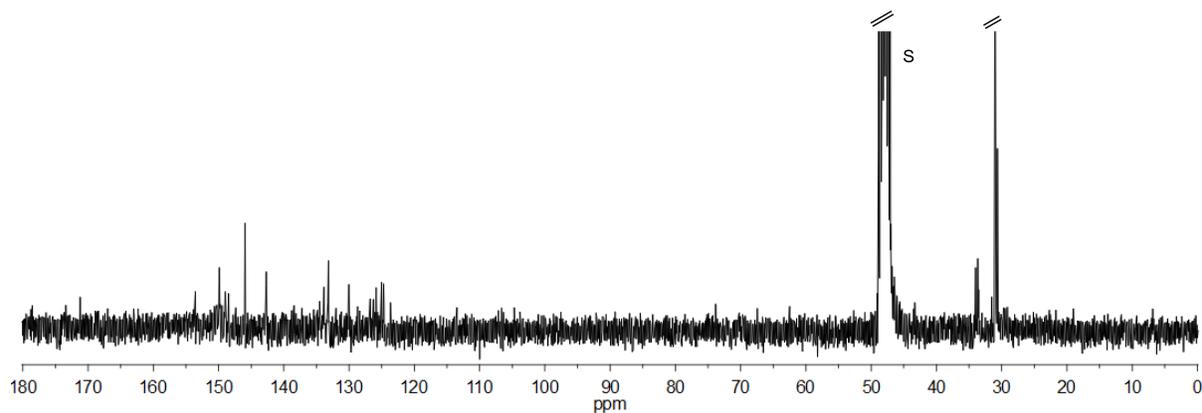
**Figure S8.** HSQC NMR spectrum (300MHz, 298K) of compound **6** in  $\text{CDCl}_3$ .



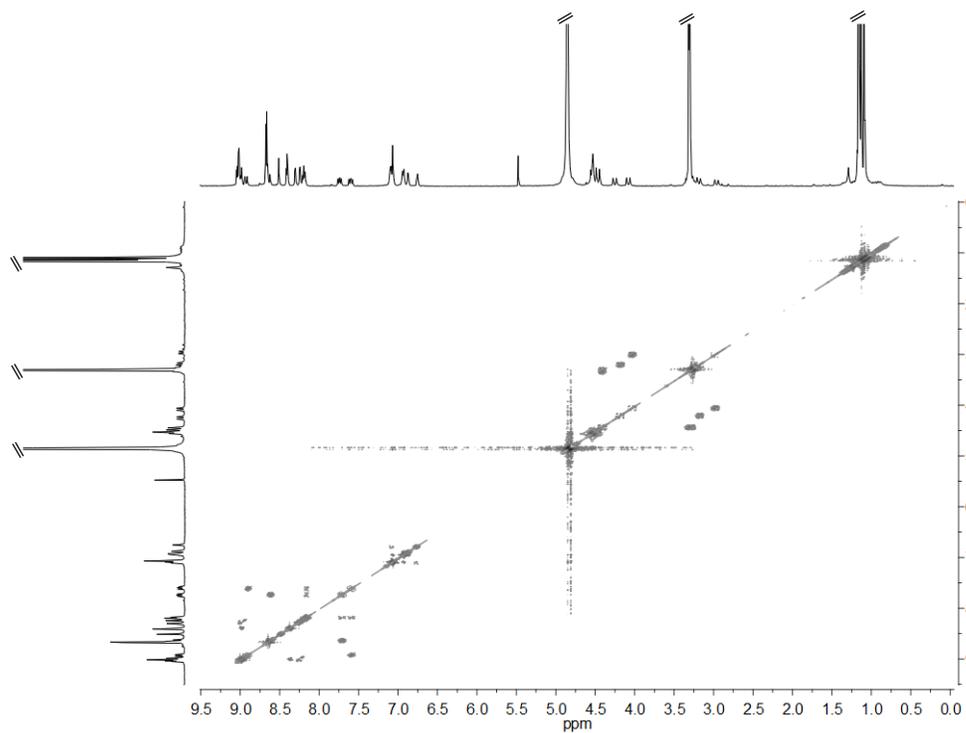
**Figure S9.**  $^1\text{H}$  NMR spectrum (300 MHz, 298K) of compound **7** in  $\text{CD}_3\text{OD}$ . S = solvent, W = water, G = grease.



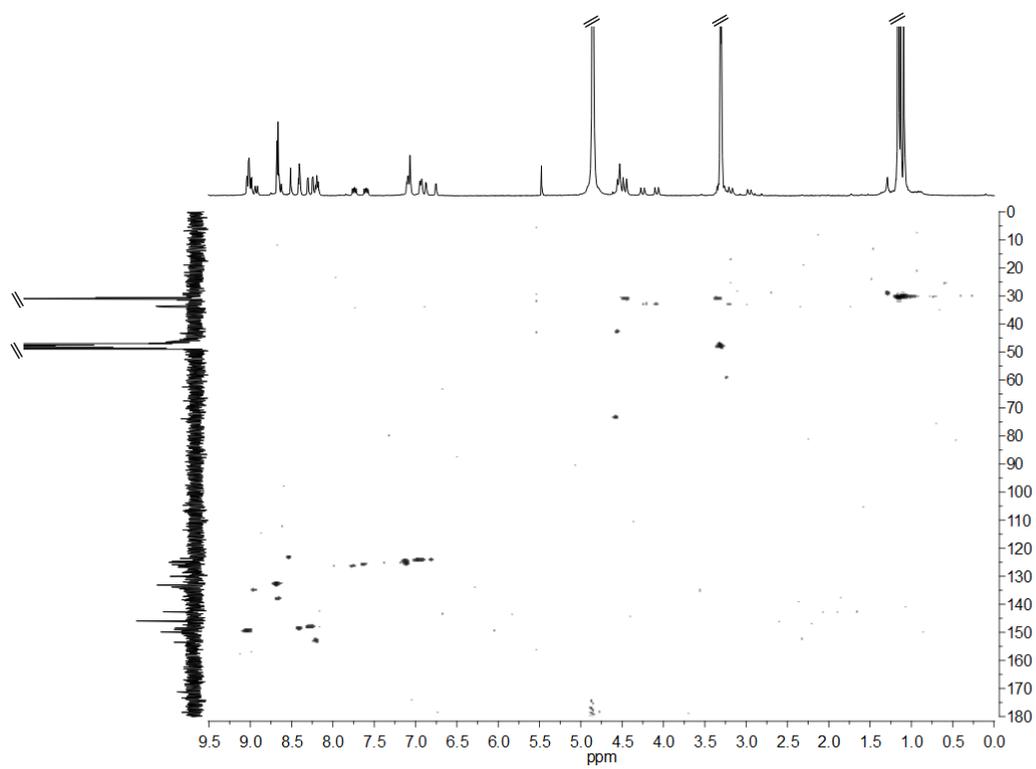
**Figure S10.**  $^{13}\text{C}$  NMR spectrum (75 MHz, 298K) of compound **7** in  $\text{CD}_3\text{OD}$ . S = solvent.



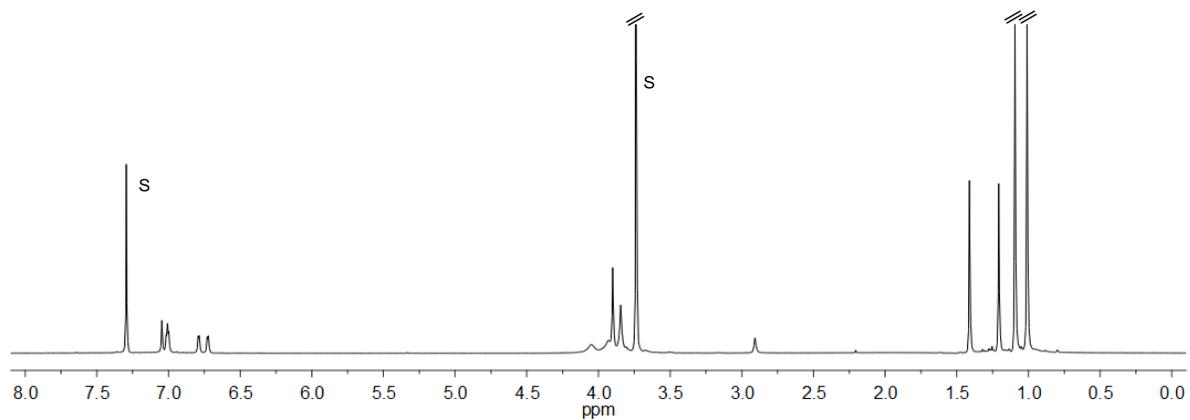
**Figure S11.** COSY NMR spectrum (300MHz, 298K) of compound **7** in CD<sub>3</sub>OD.



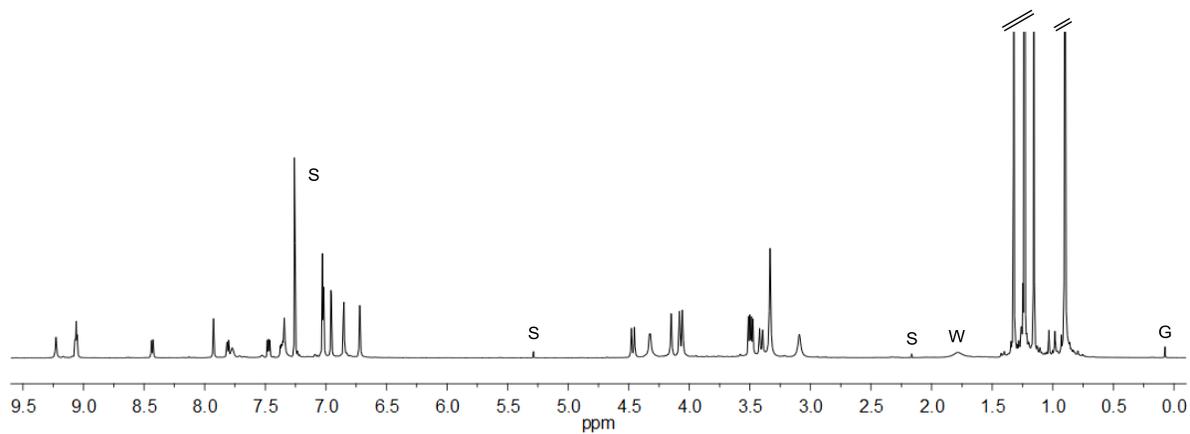
**Figure S12.** HSQC NMR spectrum (300MHz, 298K) of compound **7** in CD<sub>3</sub>OD.



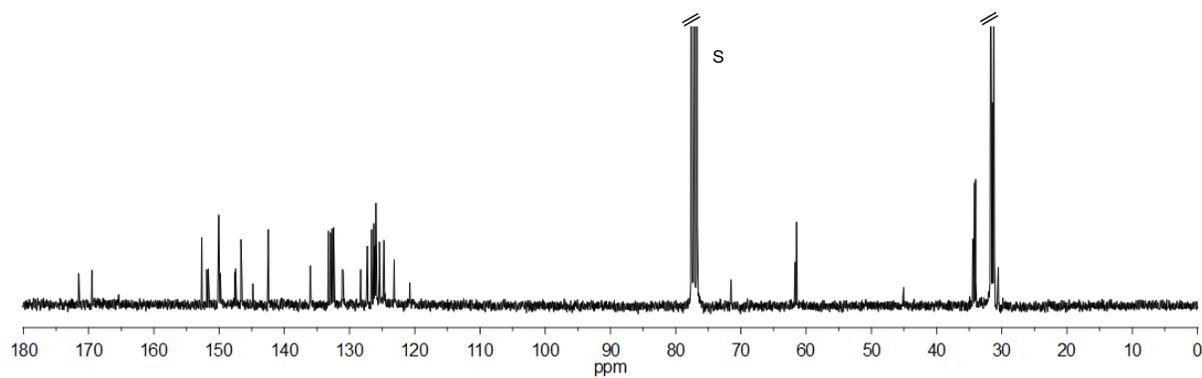
**Figure S13.**  $^1\text{H}$  NMR spectrum (300 MHz, 298K) of compound **11** in  $\text{CDCl}_3$ . S = solvent.



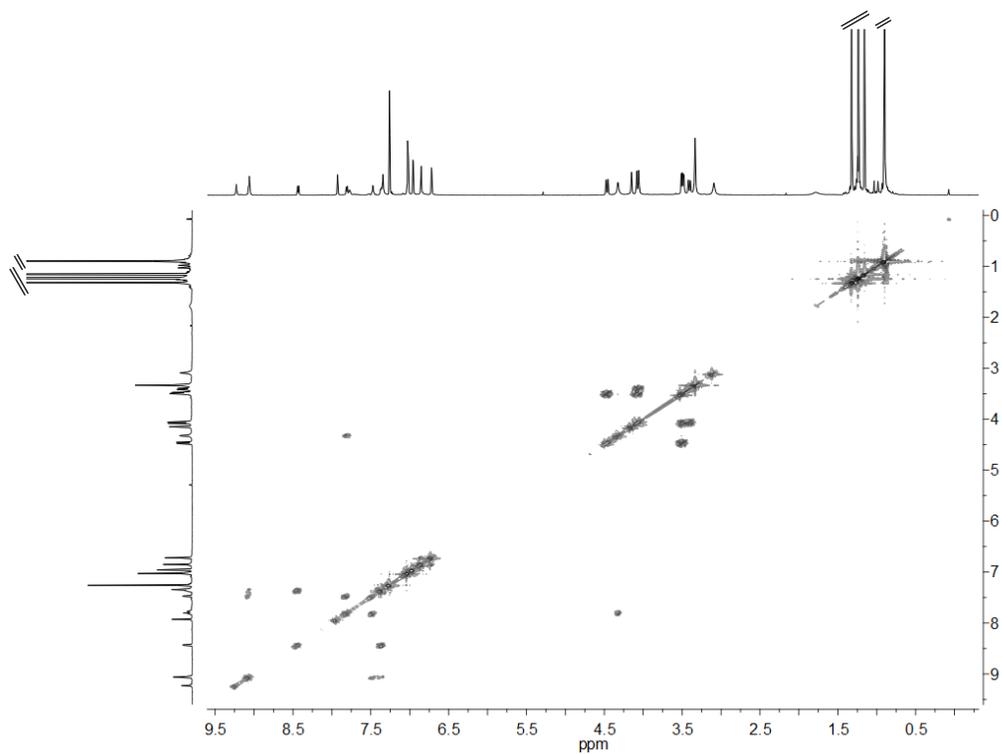
**Figure S14.**  $^1\text{H}$  NMR spectrum (600 MHz, 298K) of compound **12** in  $\text{CDCl}_3$ . S = solvent, W = water, G = grease.



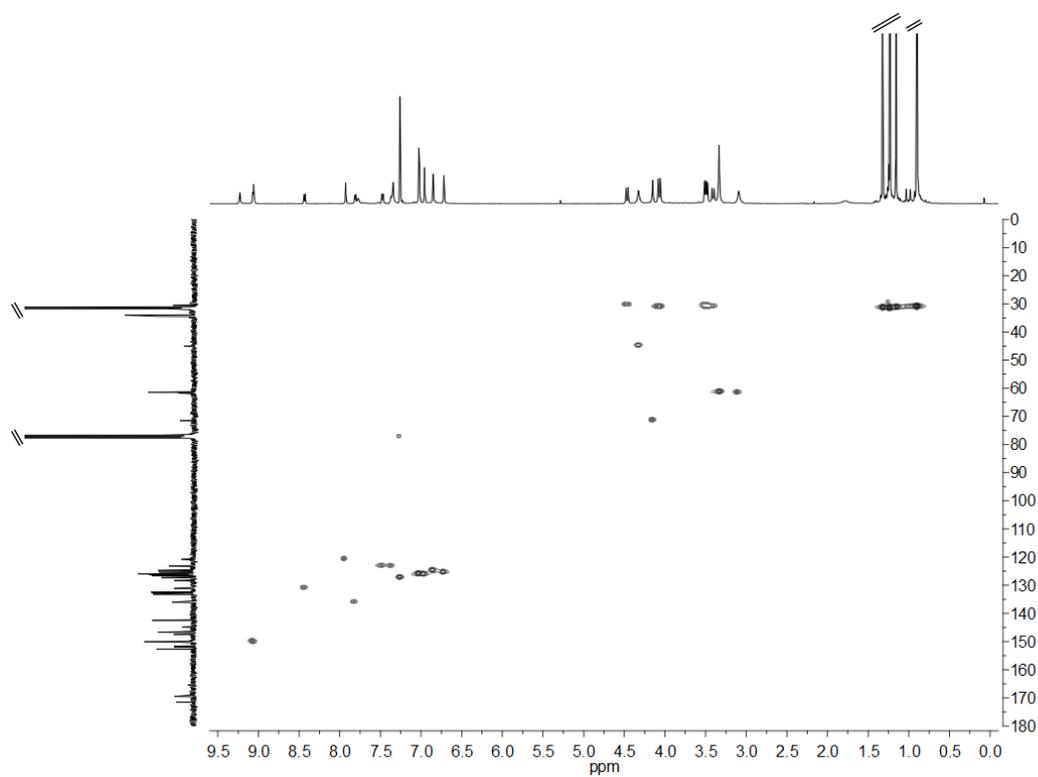
**Figure S15.**  $^{13}\text{C}$  NMR spectrum (75 MHz, 298K) of compound **12** in  $\text{CDCl}_3$ . S = solvent.



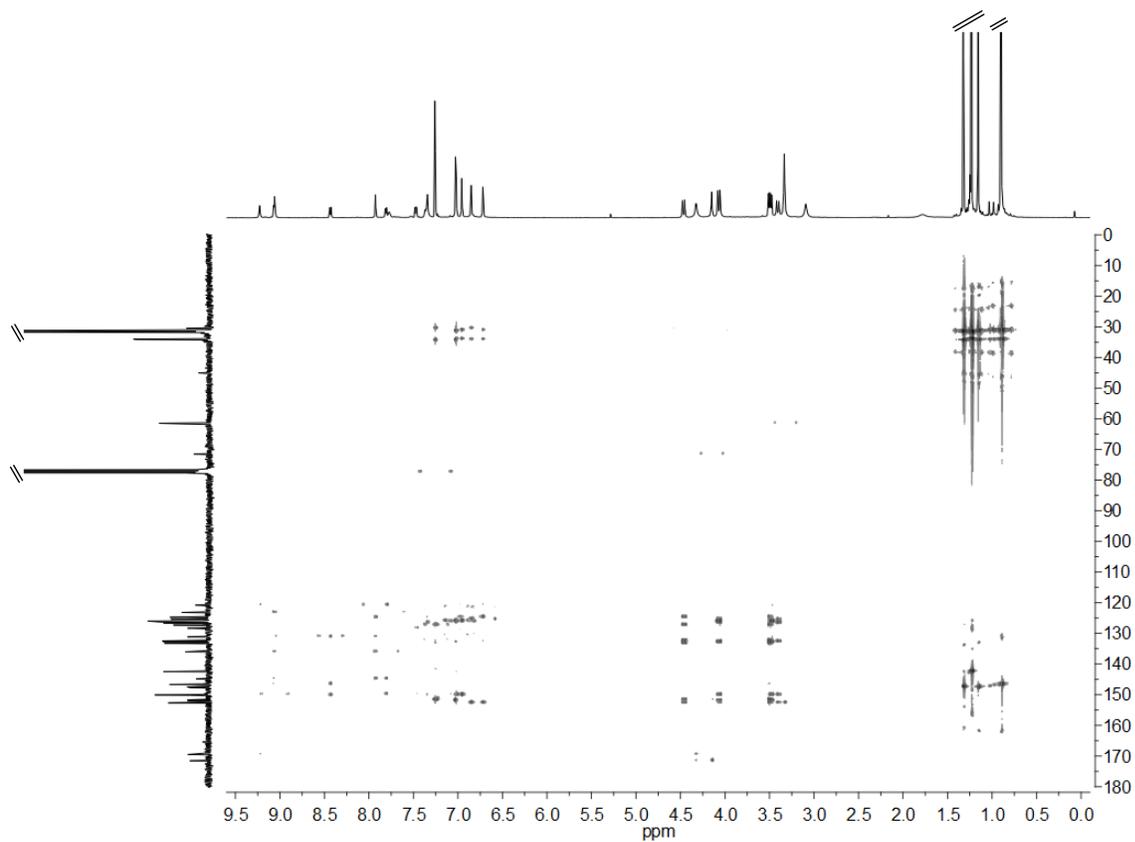
**Figure S16.** COSY NMR spectrum (300MHz, 298K) of compound **12** in CDCl<sub>3</sub>.



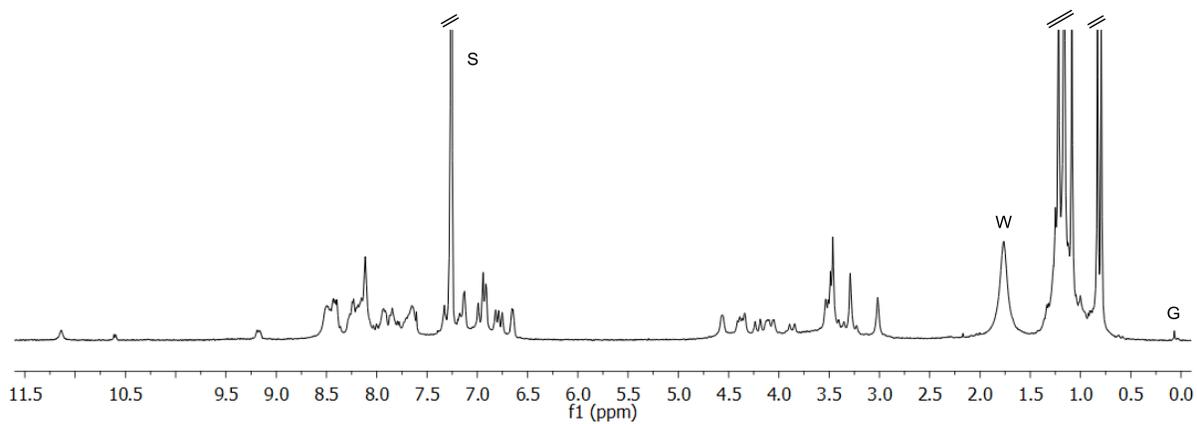
**Figure S17.** HSQC NMR spectrum (300MHz, 298K) of compound **12** in CDCl<sub>3</sub>.



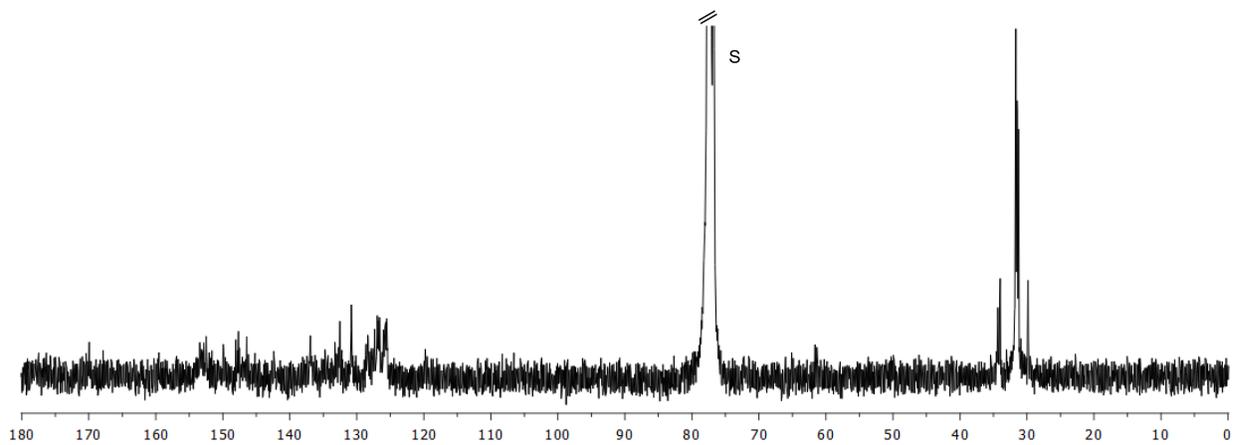
**Figure S18.** HMBC NMR spectrum (600MHz, 298K) of compound **12** in CDCl<sub>3</sub>.



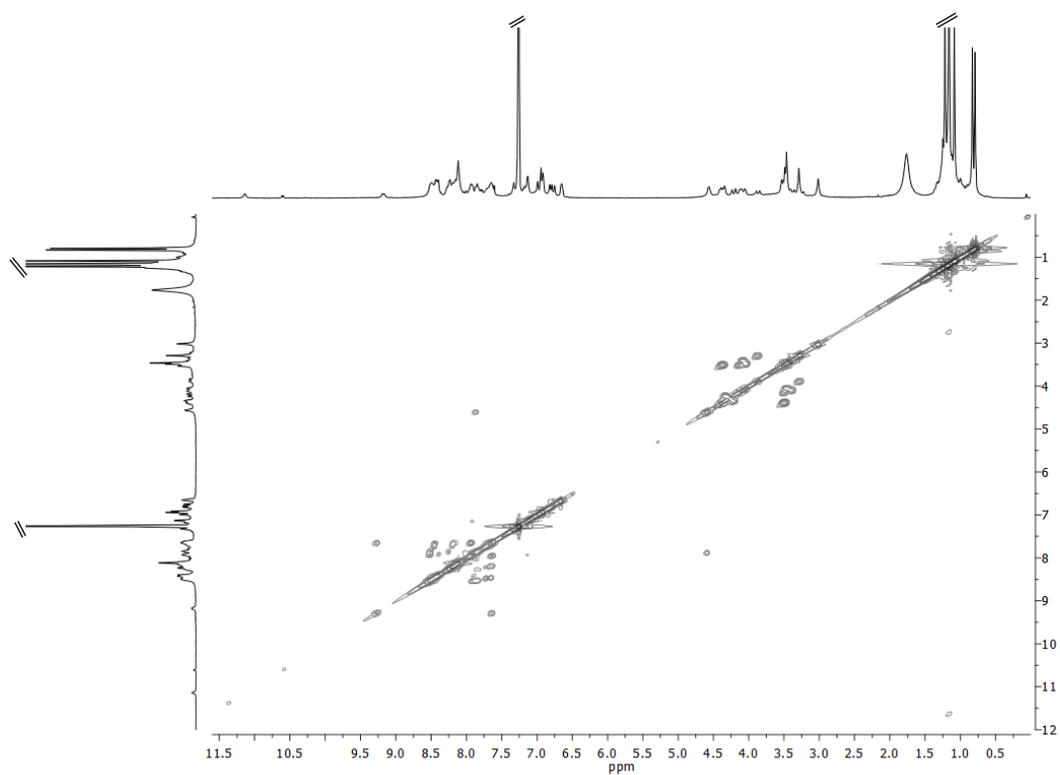
**Figure S19.**  $^1\text{H}$  NMR spectrum (300 MHz, 298K) of compound **13** in  $\text{CDCl}_3$ . S = solvent, W = water, G = grease.



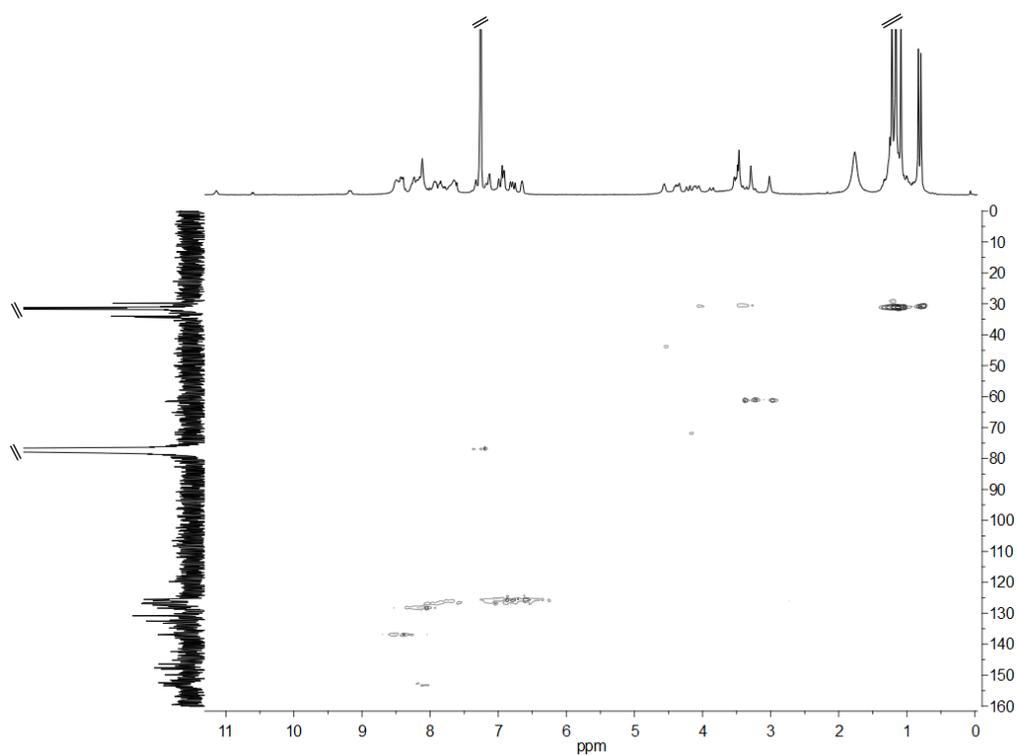
**Figure S20.**  $^{13}\text{C}$  NMR spectrum (75 MHz, 298K) of compound **13** in  $\text{CDCl}_3$ . S = solvent.



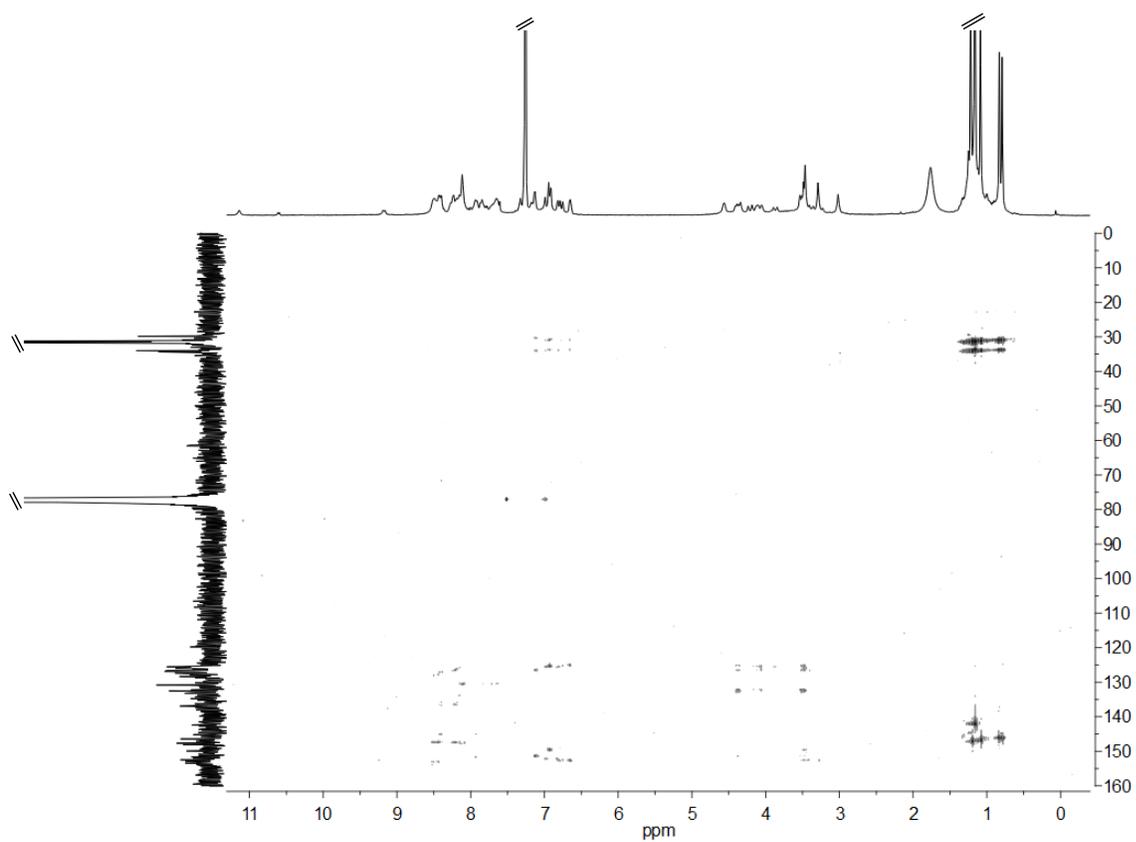
**Figure S21.** COSY NMR spectrum (300MHz, 298K) of compound **13** in  $\text{CDCl}_3$ .



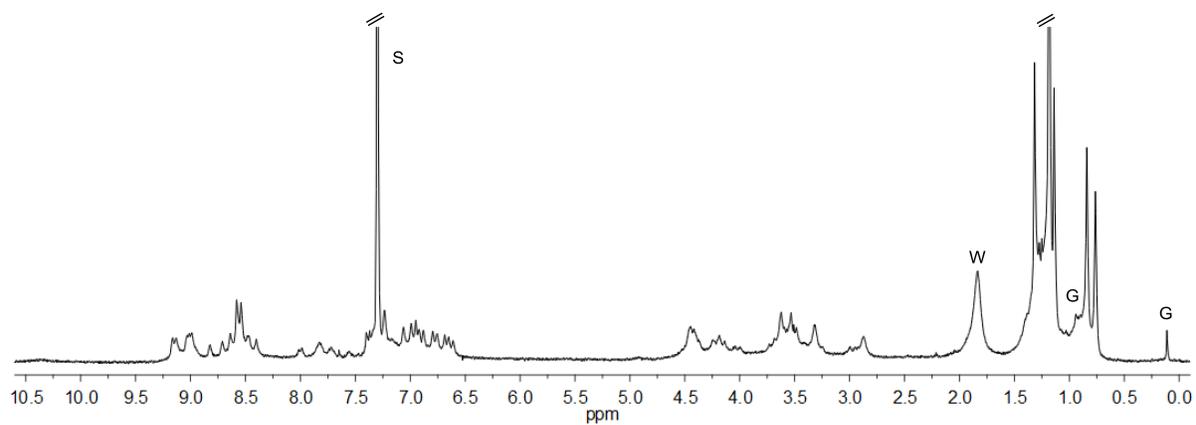
**Figure S22.** HSQC NMR spectrum (300MHz, 298K) of compound **13** in  $\text{CDCl}_3$ .



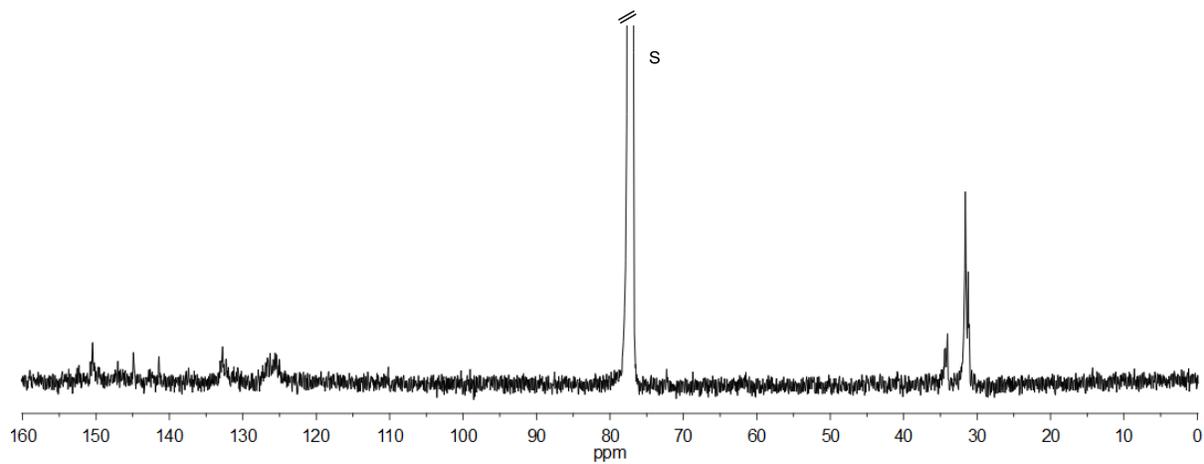
**Figure S23.** HMBC NMR spectrum (400MHz, 298K) of compound **13** in CDCl<sub>3</sub>.



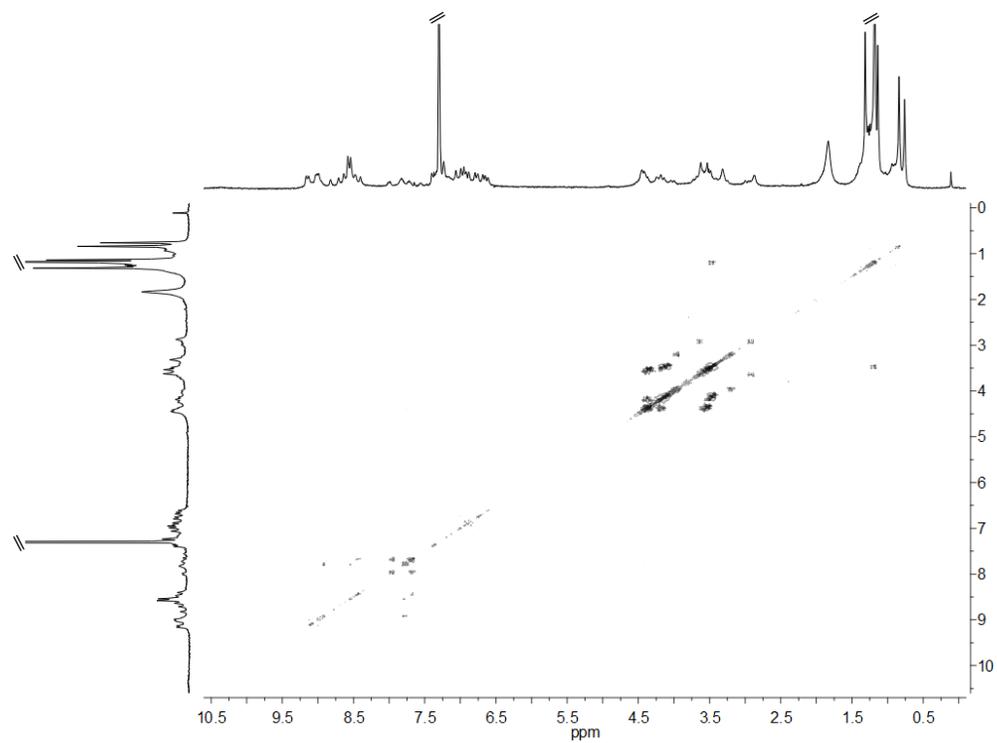
**Figure S24.**  $^1\text{H}$  NMR spectrum (300 MHz, 298K) of compound **14** in  $\text{CDCl}_3$ . S = solvent, W = water, G = grease.



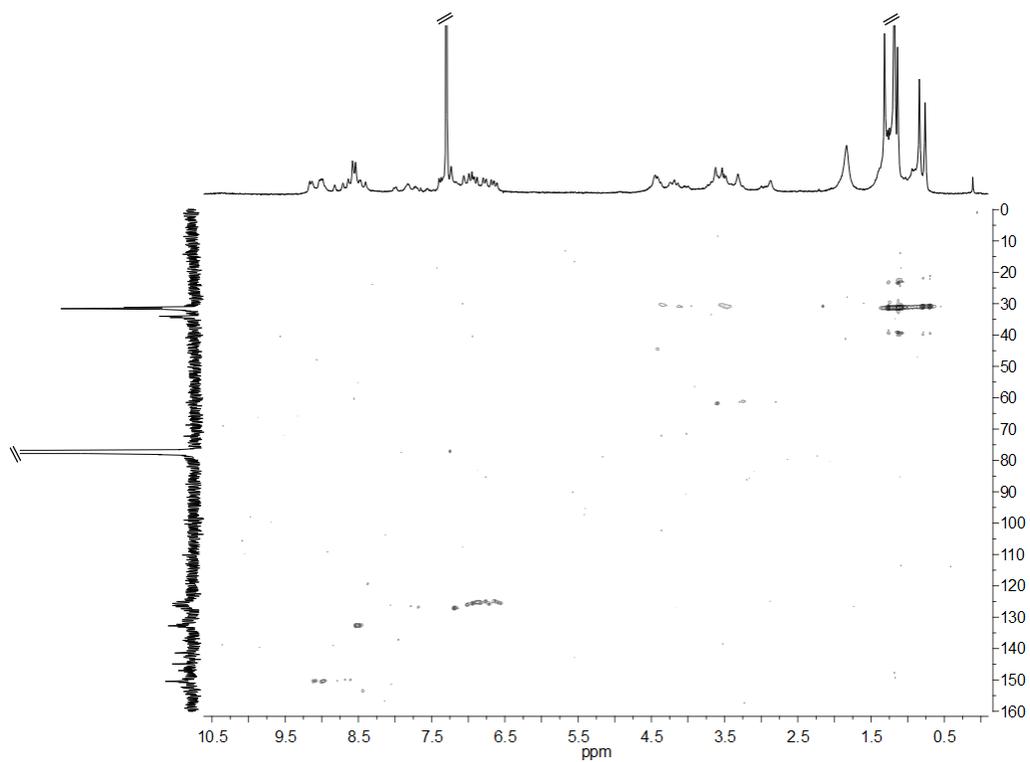
**Figure S25.**  $^{13}\text{C}$  NMR spectrum (100 MHz, 298K) of compound **14** in  $\text{CDCl}_3$ . S = solvent.



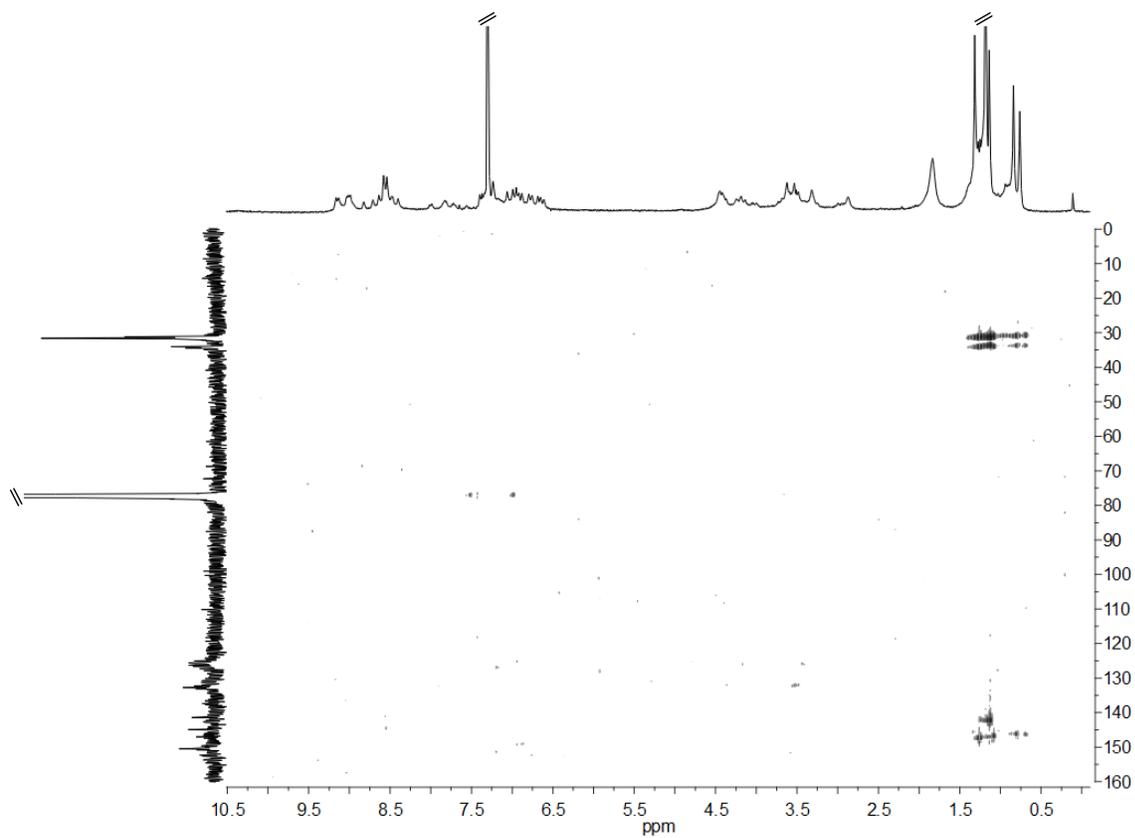
**Figure S26.** COSY NMR spectrum (400MHz, 298K) of compound **14** in CDCl<sub>3</sub>.



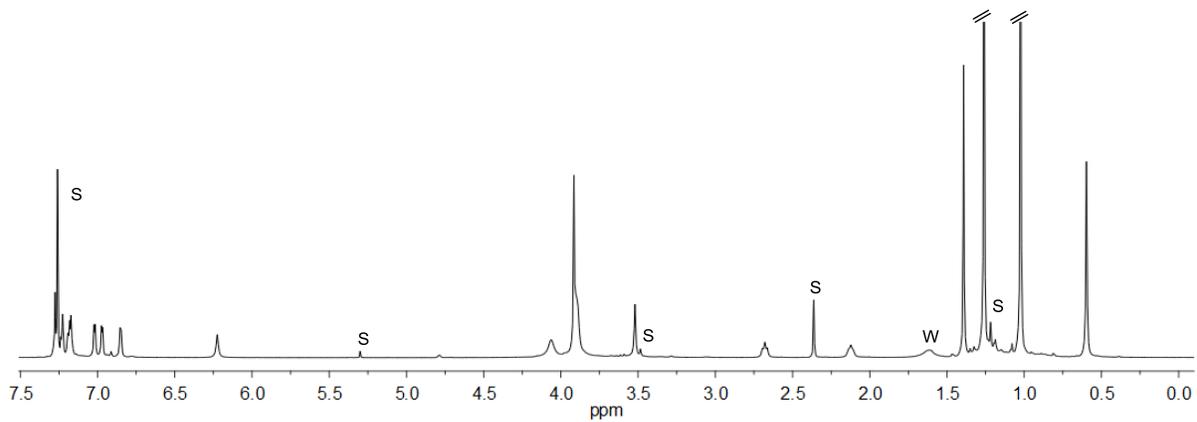
**Figure S27.** HSQC NMR spectrum (400MHz, 298K) of compound **14** in CDCl<sub>3</sub>.



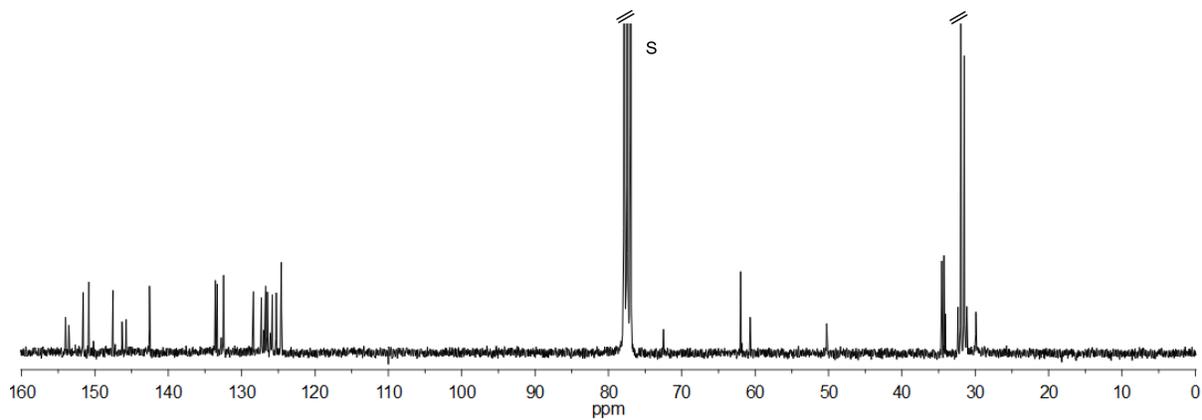
**Figure S28.** HMBC NMR spectrum (400MHz, 298K) of compound **14** in  $\text{CDCl}_3$ .



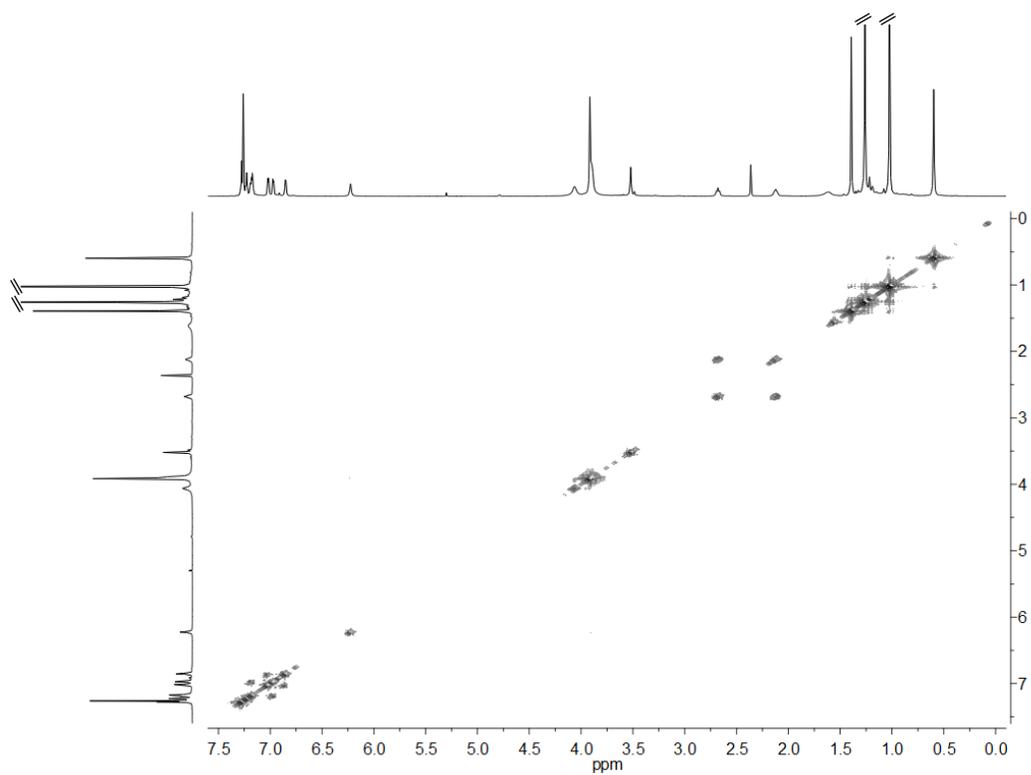
**Figure S29.**  $^1\text{H}$  NMR spectrum (300 MHz, 298K) of compound **17** in  $\text{CDCl}_3$ . S = solvent, W = water.



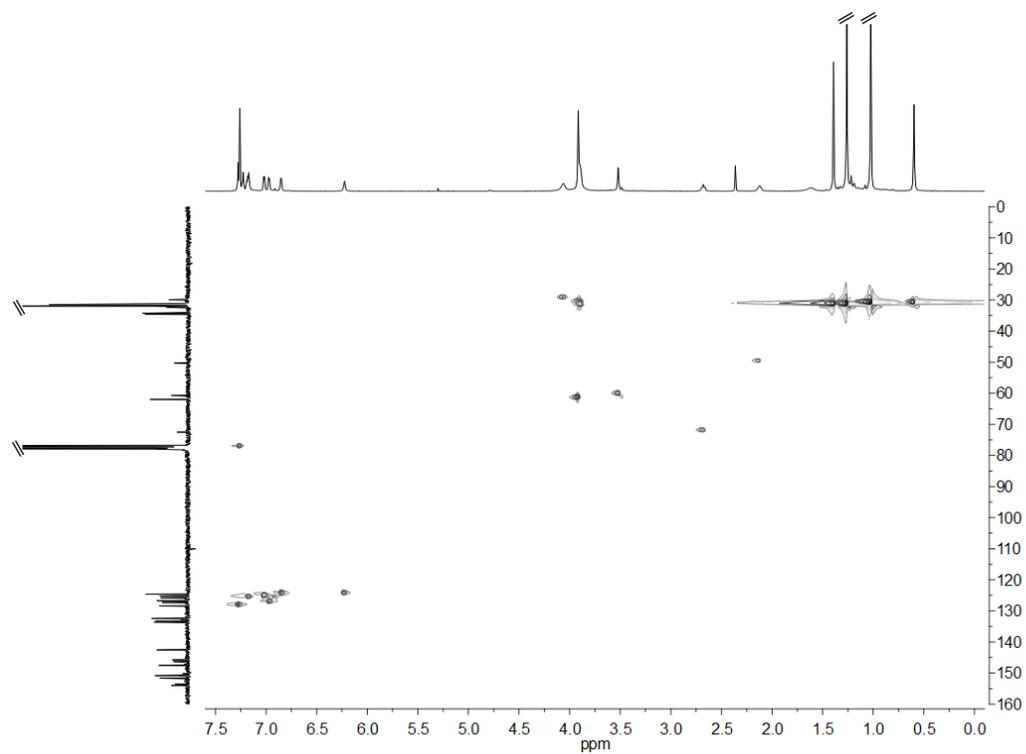
**Figure S30.**  $^{13}\text{C}$  NMR spectrum (75 MHz, 298K) of compound **17** in  $\text{CDCl}_3$ . S = solvent.



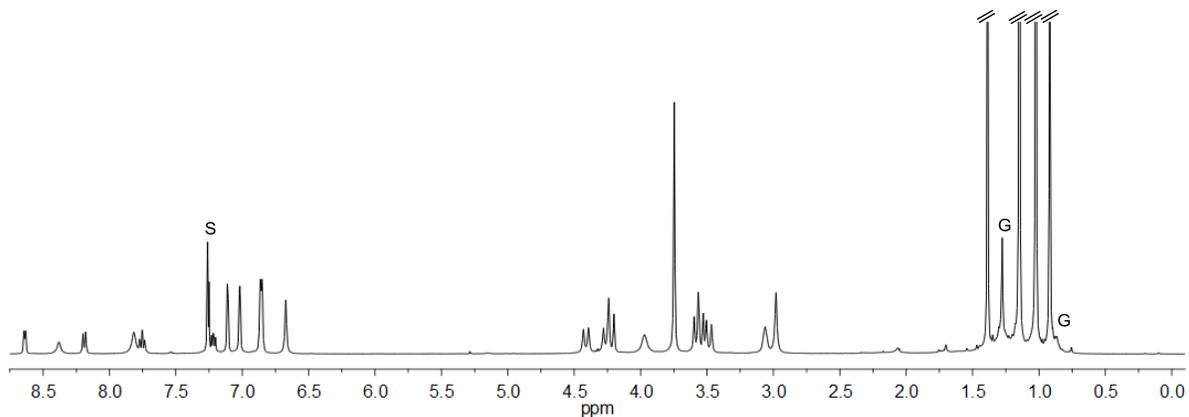
**Figure S31.** COSY NMR spectrum (300MHz, 298K) of compound **17** in CDCl<sub>3</sub>.



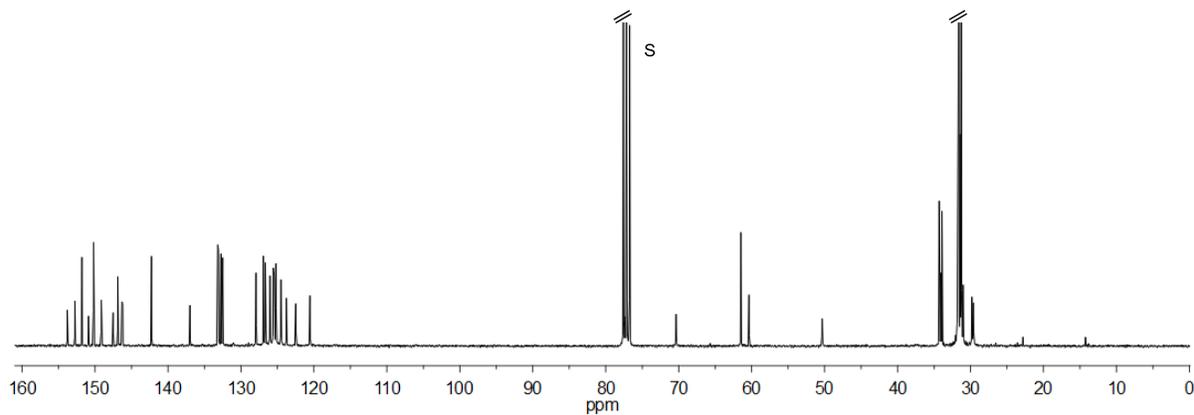
**Figure S32.** HSQC NMR spectrum (300MHz, 298K) of compound **17** in CDCl<sub>3</sub>.



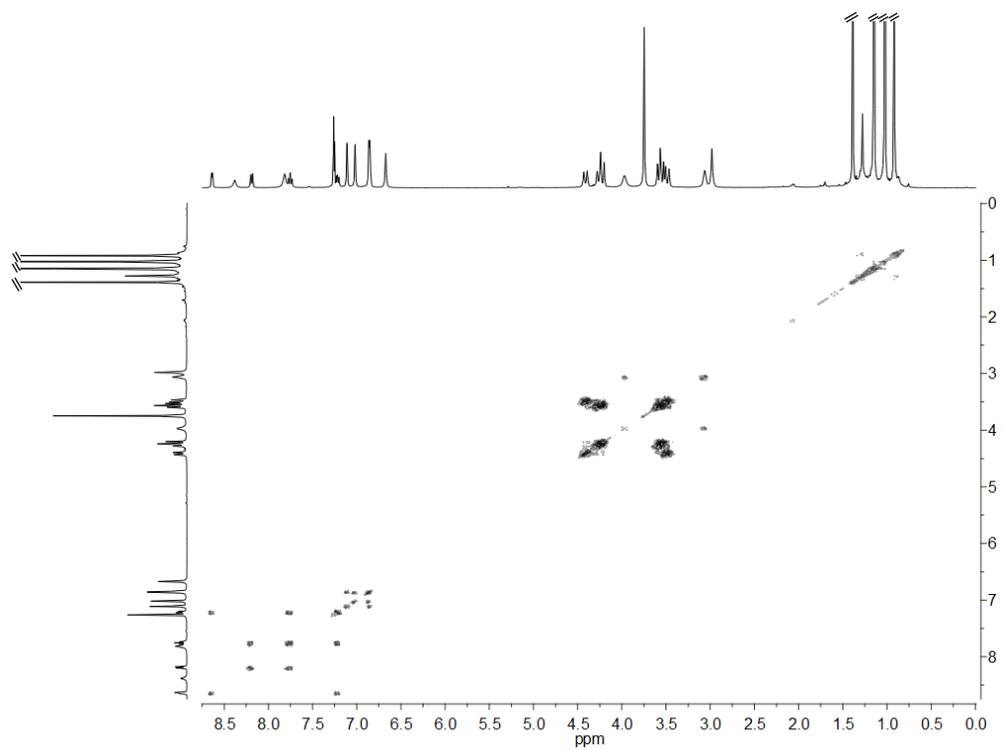
**Figure S33.**  $^1\text{H}$  NMR spectrum (400 MHz, 298K) of compound **18** in  $\text{CDCl}_3$ . S = solvent, G = grease.



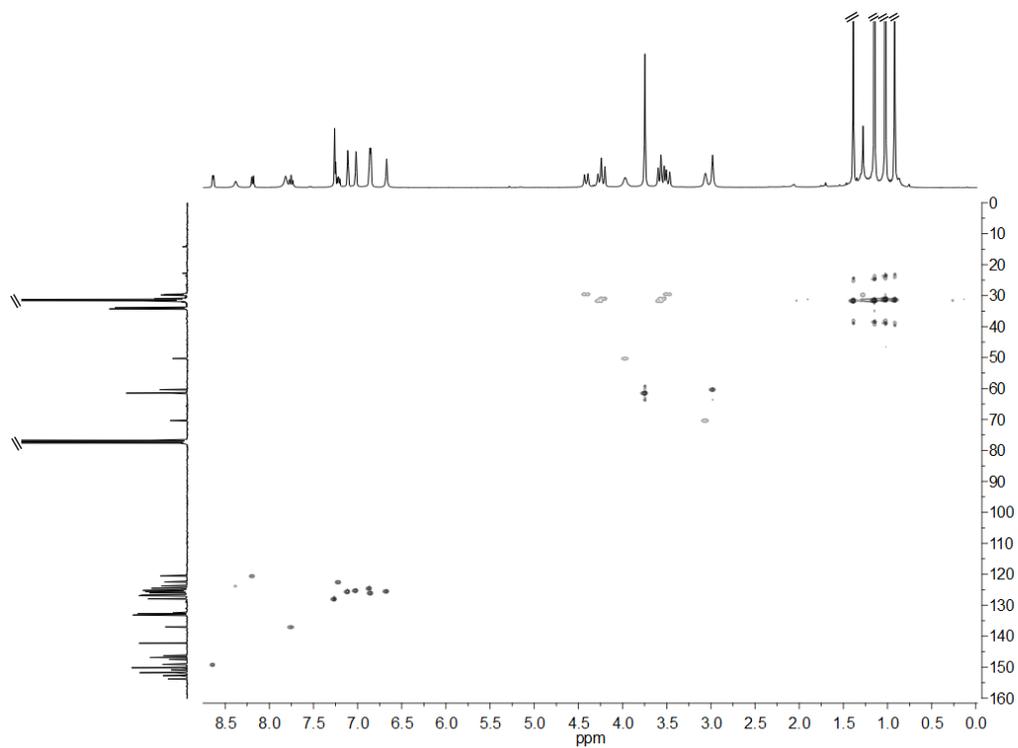
**Figure S34.**  $^{13}\text{C}$  NMR spectrum (75 MHz, 298K) of compound **18** in  $\text{CDCl}_3$ . S = solvent.



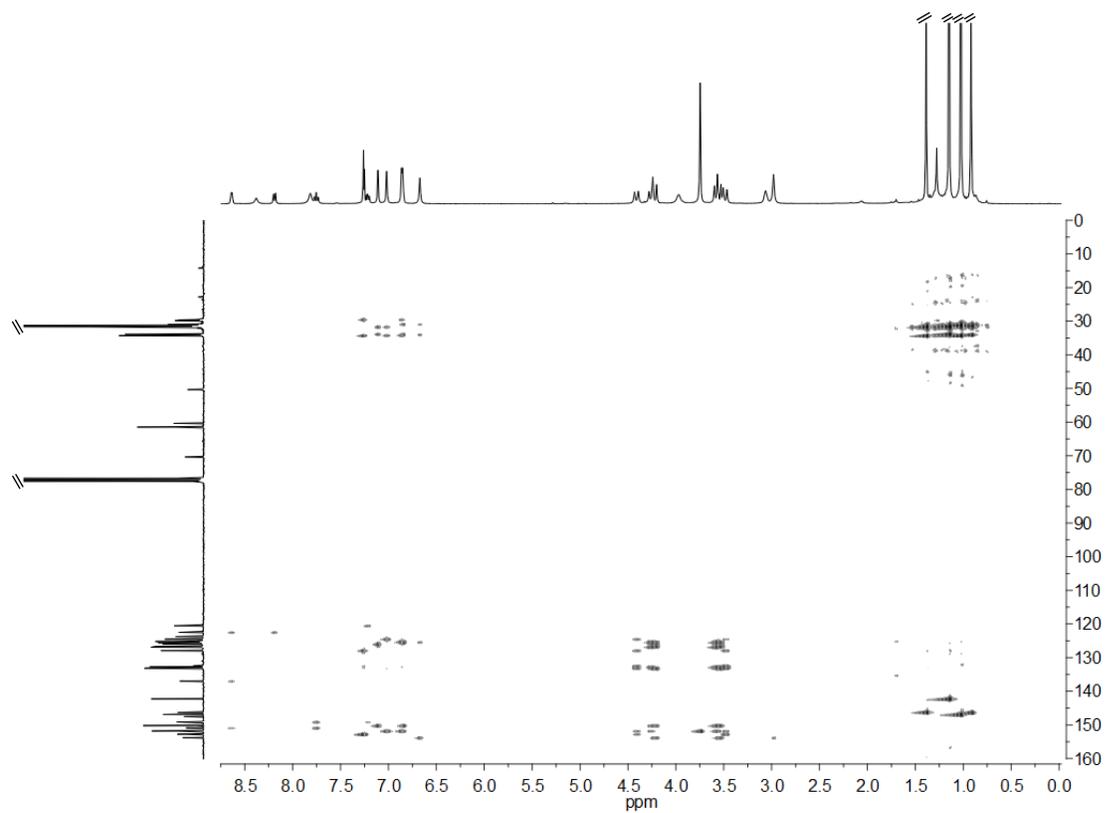
**Figure S35.** COSY NMR spectrum (400MHz, 298K) of compound **18** in CDCl<sub>3</sub>.



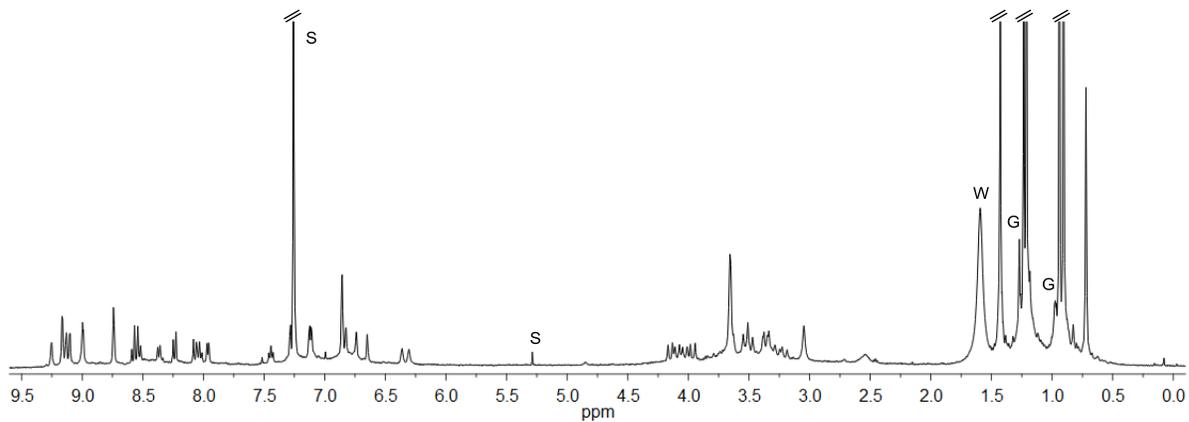
**Figure S36.** HSQC NMR spectrum (400MHz, 298K) of compound **18** in CDCl<sub>3</sub>.



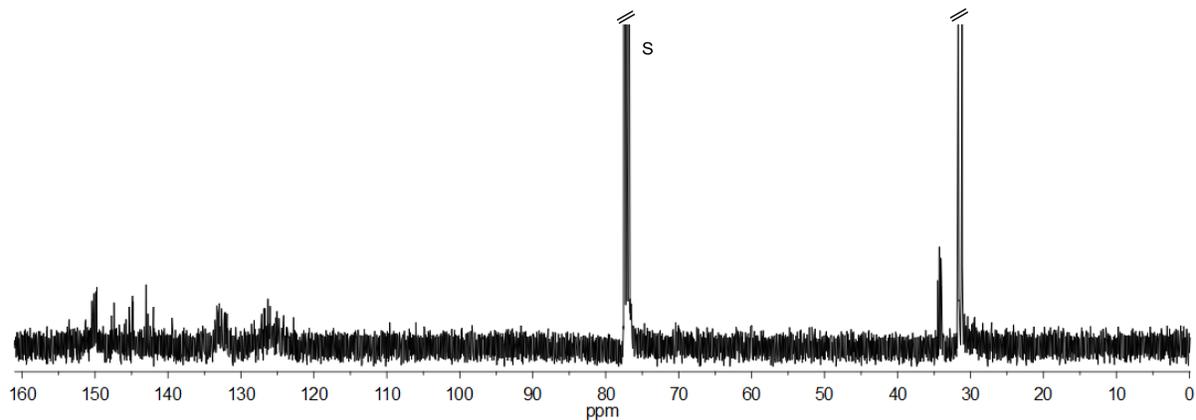
**Figure S37.** HMBC NMR spectrum (400MHz, 298K) of compound **18** in  $\text{CDCl}_3$ .



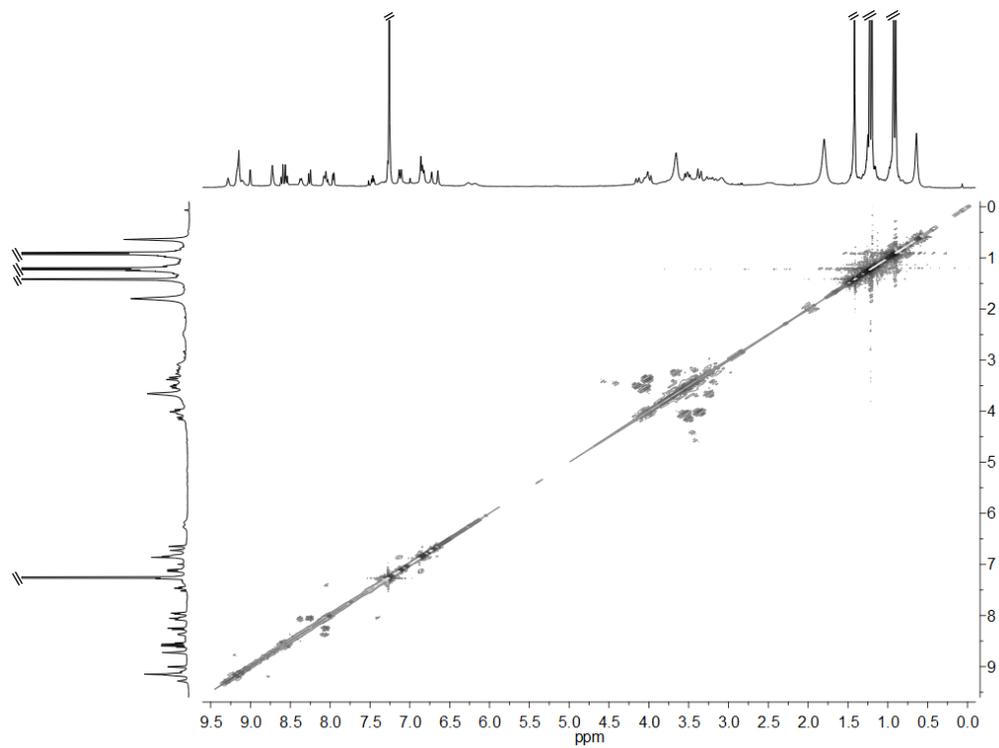
**Figure S38.**  $^1\text{H}$  NMR spectrum (400 MHz, 328K) of compound **19** in  $\text{CDCl}_3$ . S = solvent, W = water, G = grease.



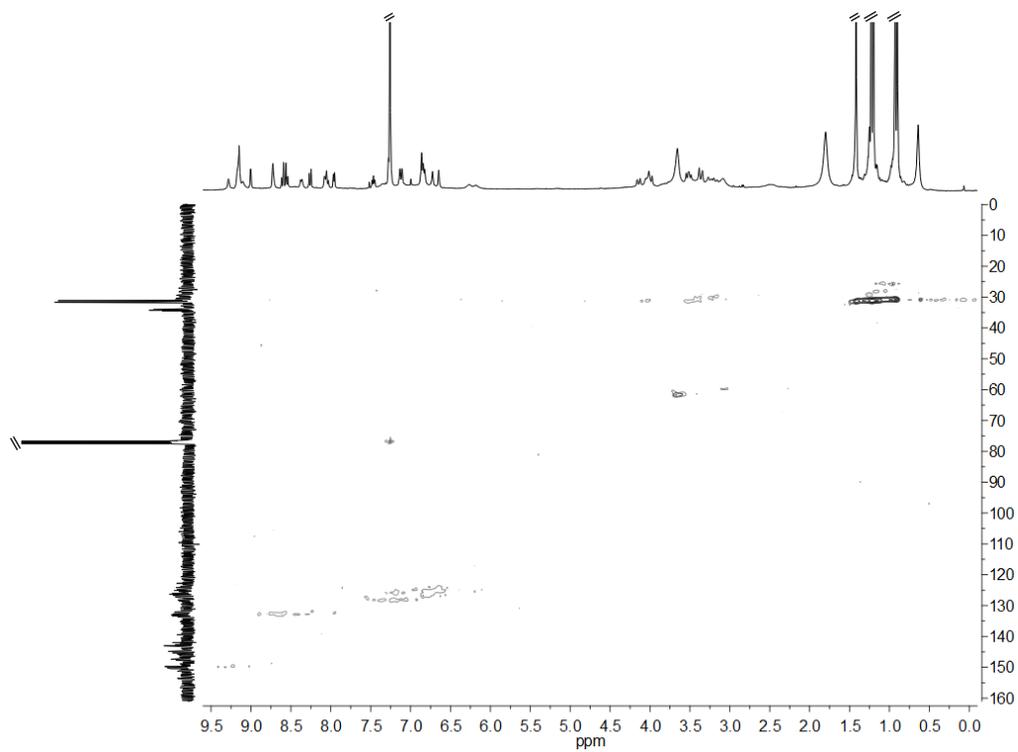
**Figure S39.**  $^{13}\text{C}$  NMR spectrum (100 MHz, 298K) of compound **19** in  $\text{CDCl}_3$ . S = solvent.



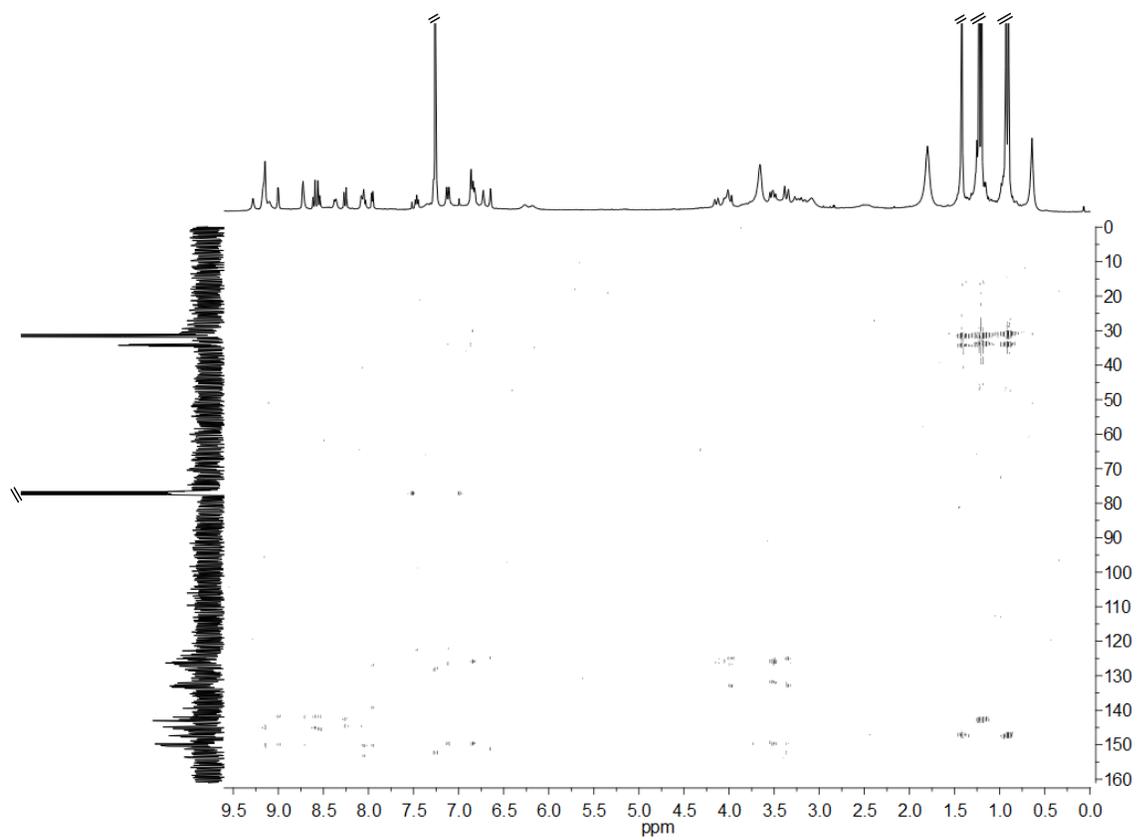
**Figure S40.** COSY NMR spectrum (400MHz, 298K) of compound **19** in CDCl<sub>3</sub>.



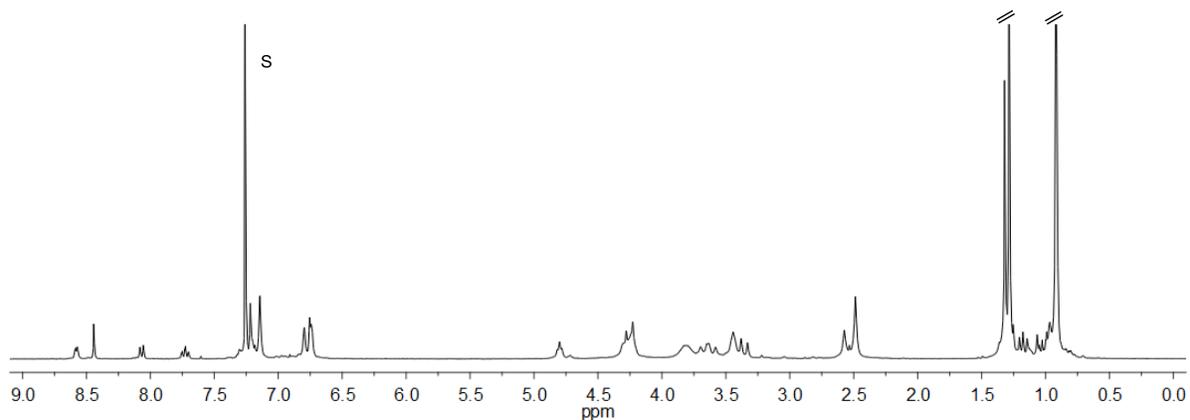
**Figure S41.** HSQC NMR spectrum (400MHz, 298K) of compound **19** in CDCl<sub>3</sub>.



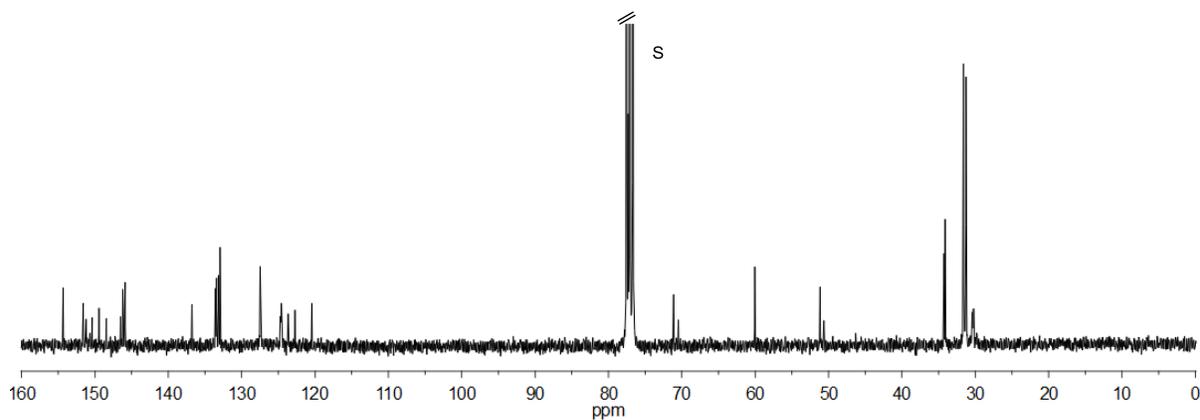
**Figure S42.** HMBC NMR spectrum (400MHz, 298K) of compound **19** in  $\text{CDCl}_3$ .



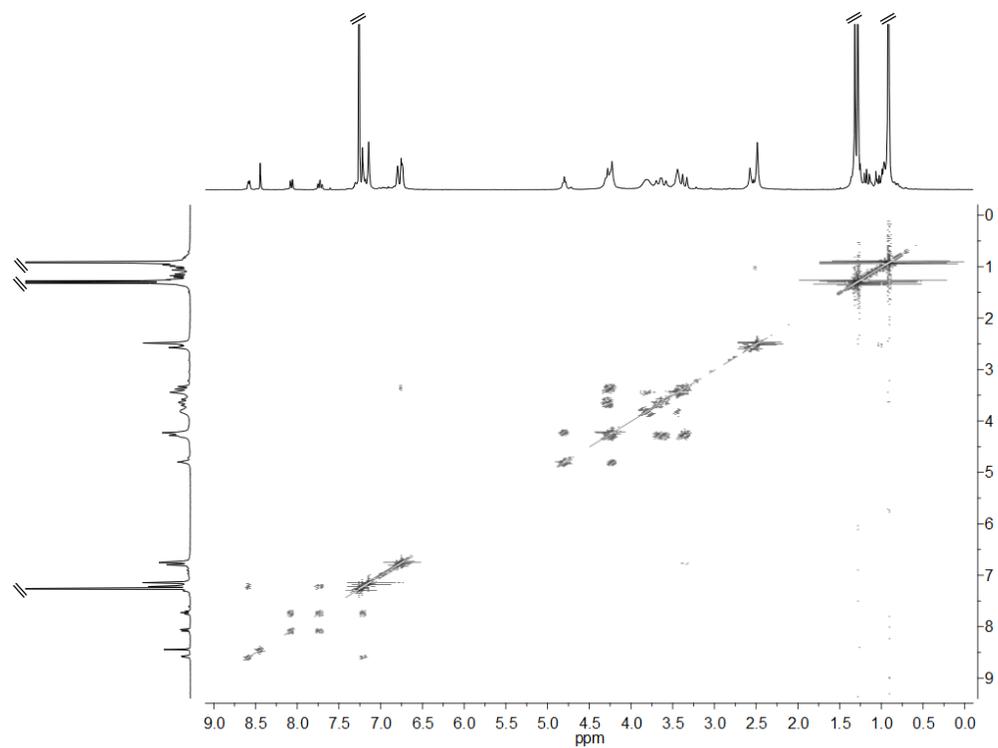
**Figure S43.**  $^1\text{H}$  NMR spectrum (300 MHz, 298K) of compound **23** in  $\text{CDCl}_3$ . S = solvent.



**Figure S44.**  $^{13}\text{C}$  NMR spectrum (75 MHz, 298K) of compound **23** in  $\text{CDCl}_3$ . S = solvent.



**Figure S45.** COSY NMR spectrum (300MHz, 298K) of compound **23** in CDCl<sub>3</sub>.



**Figure S46.** HSQC NMR spectrum (300MHz, 298K) of compound **23** in CDCl<sub>3</sub>.

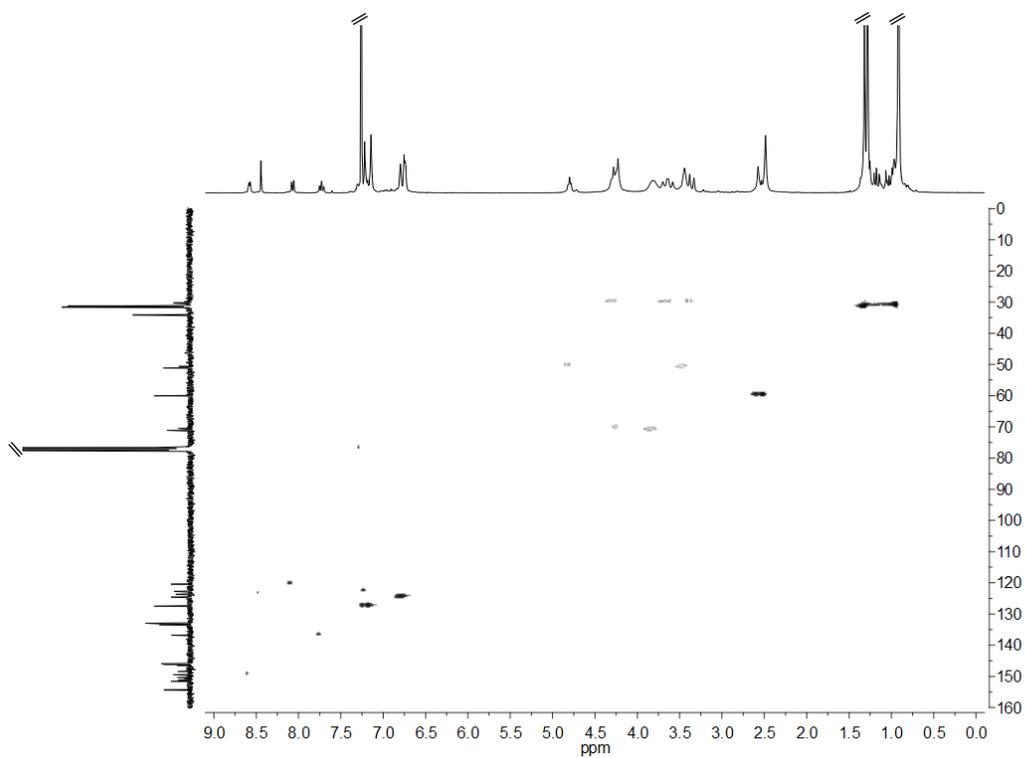
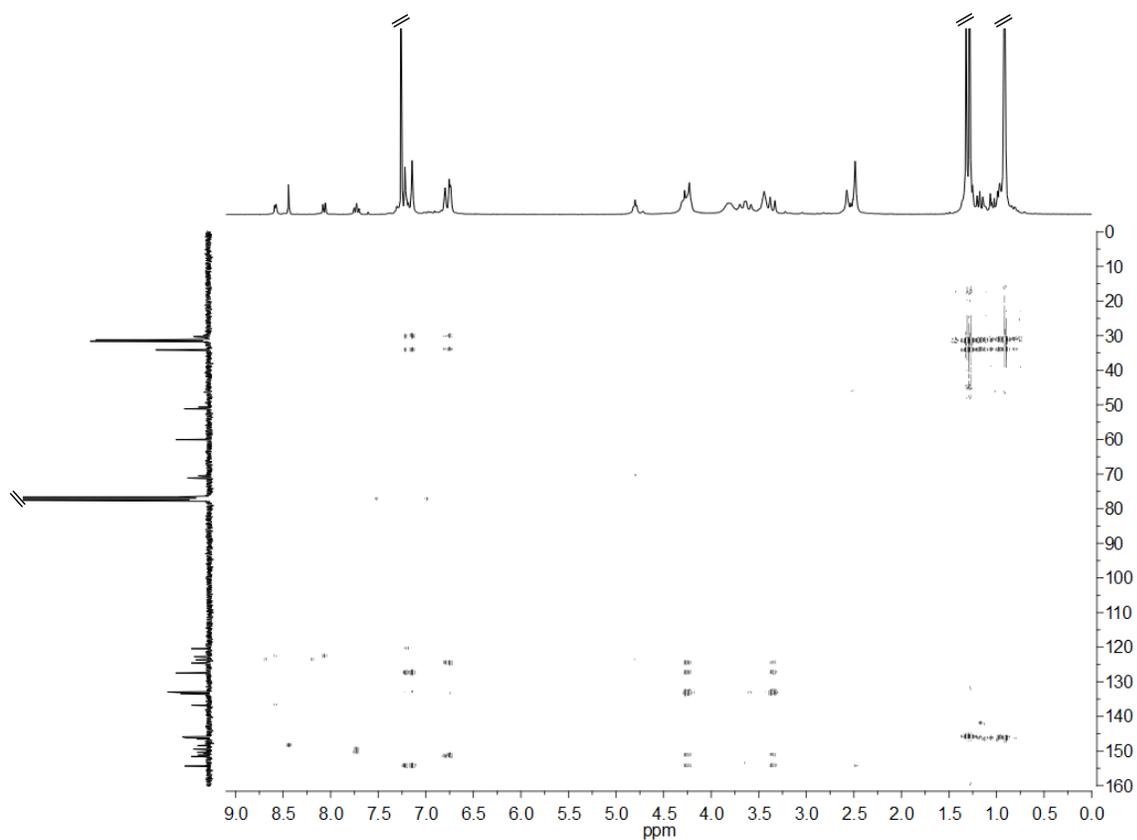
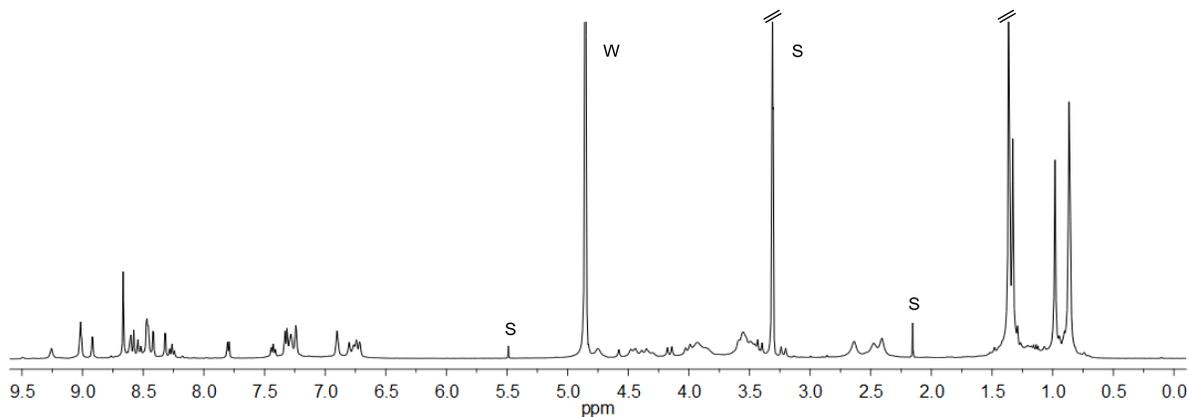


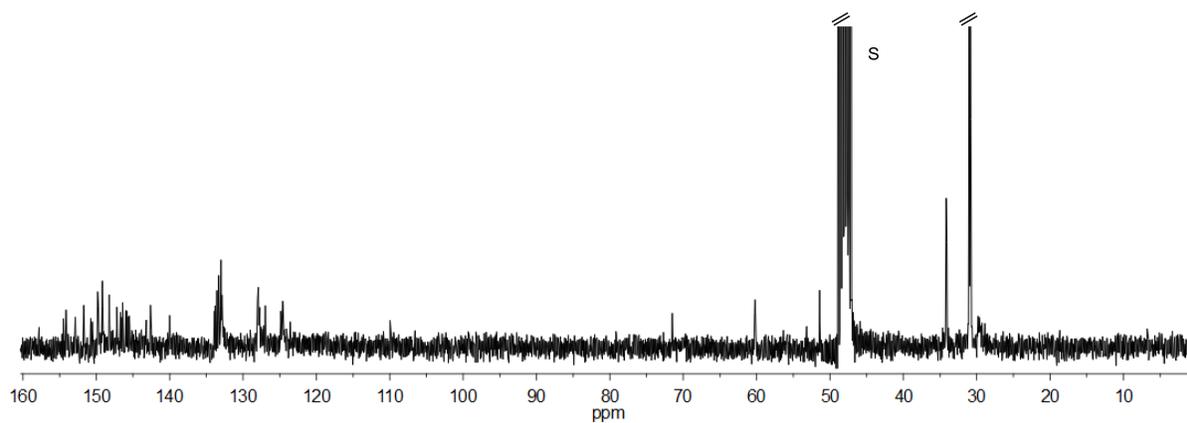
Figure S47. HMBC NMR spectrum (400MHz, 298K) of compound **23** in CDCl<sub>3</sub>.



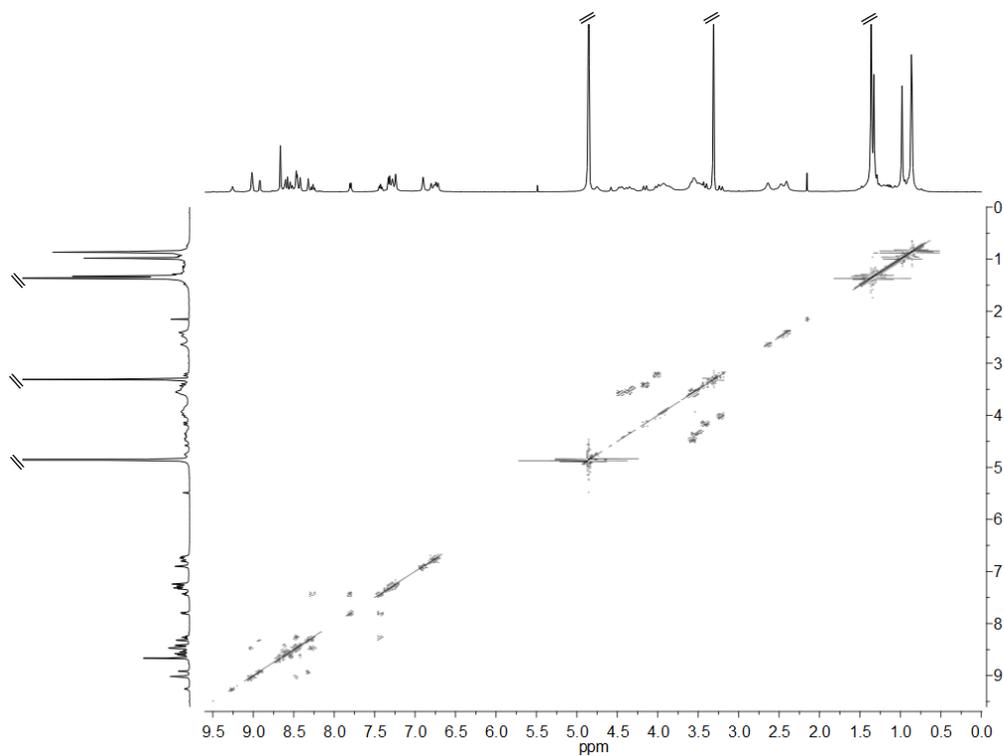
**Figure S48.**  $^1\text{H}$  NMR spectrum (400 MHz, 298K) of compound **24** in  $\text{CD}_3\text{OD}$ . S = solvent and W = water.



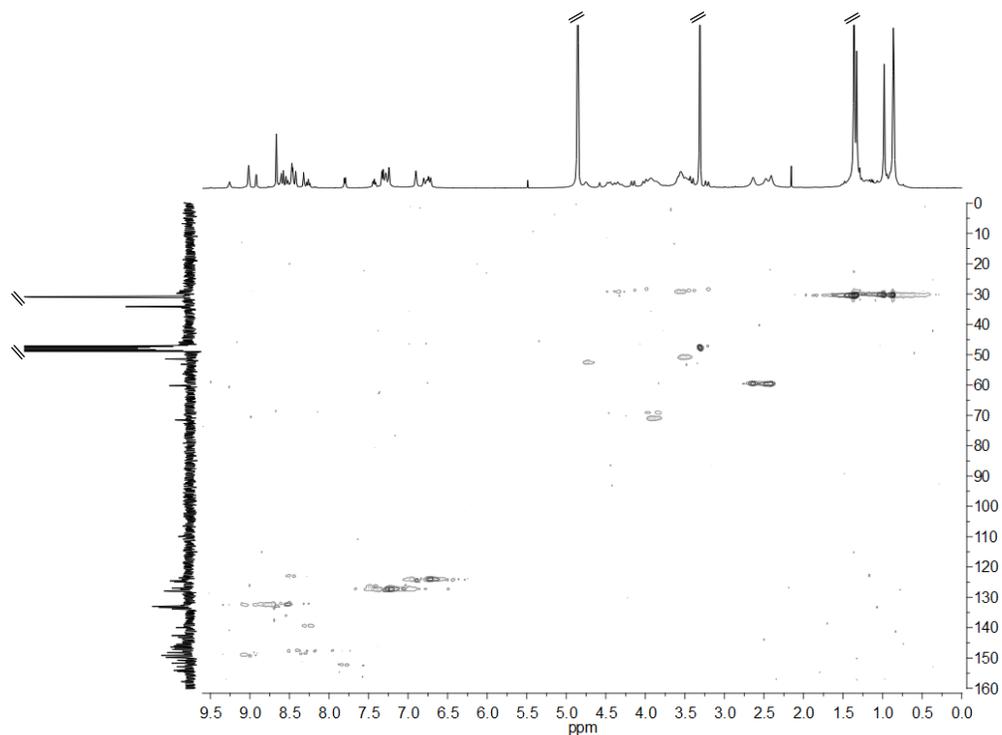
**Figure S49.**  $^{13}\text{C}$  NMR spectrum (75 MHz, 298K) of compound **24** in  $\text{CD}_3\text{OD}$ . S = solvent.



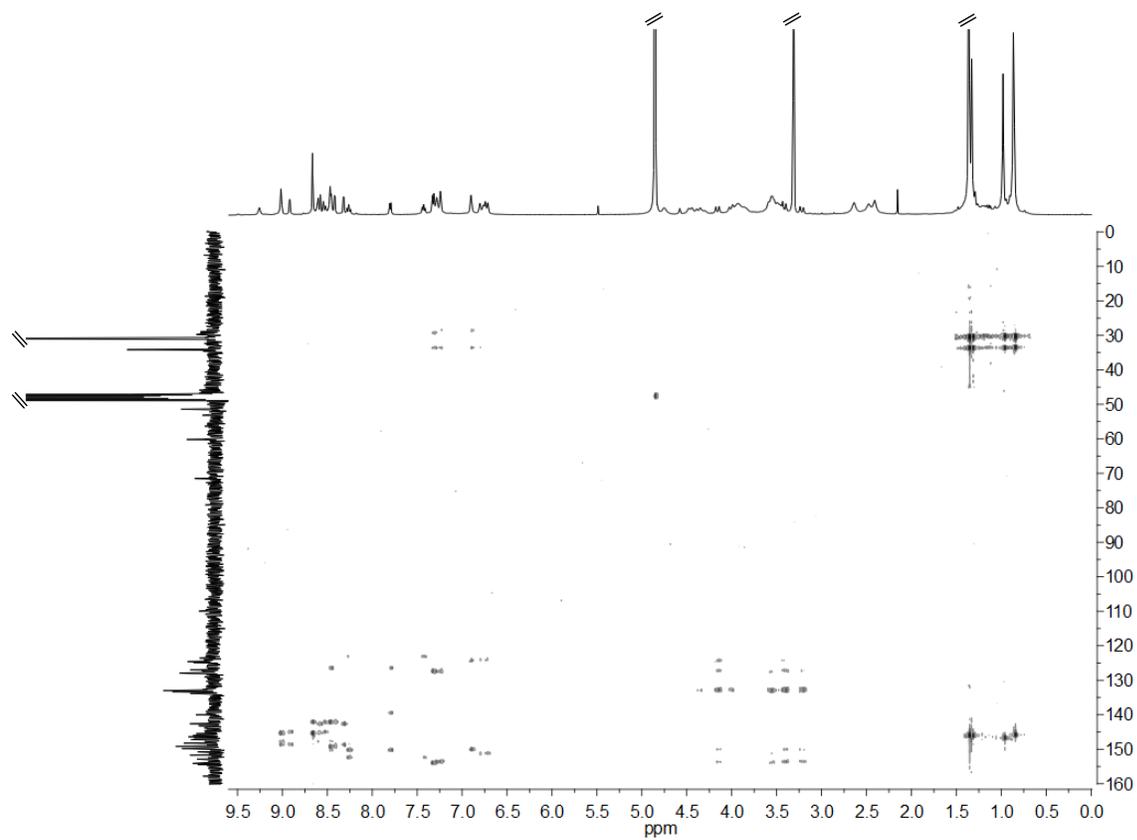
**Figure S50.** COSY NMR spectrum (300MHz, 298K) of compound **24** in CD<sub>3</sub>OD.



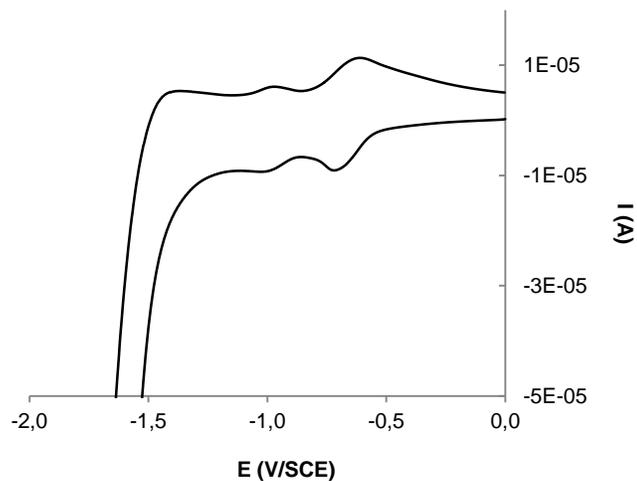
**Figure S51.** HSQC NMR spectrum (300MHz, 298K) of compound **24** in CD<sub>3</sub>OD.



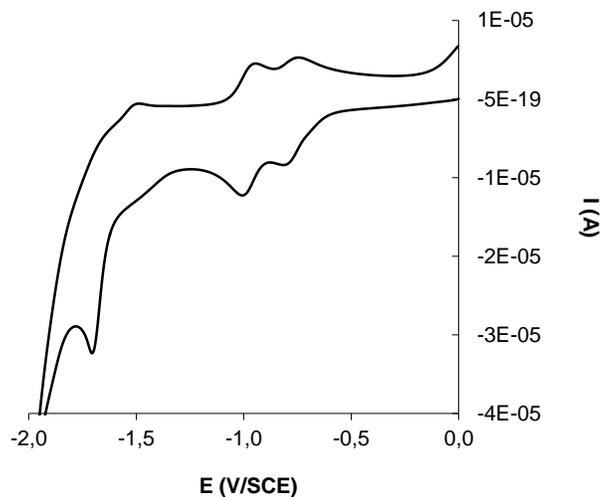
**Figure S52.** HMBC NMR spectrum (400MHz, 298K) of compound **24** in CD<sub>3</sub>OD.



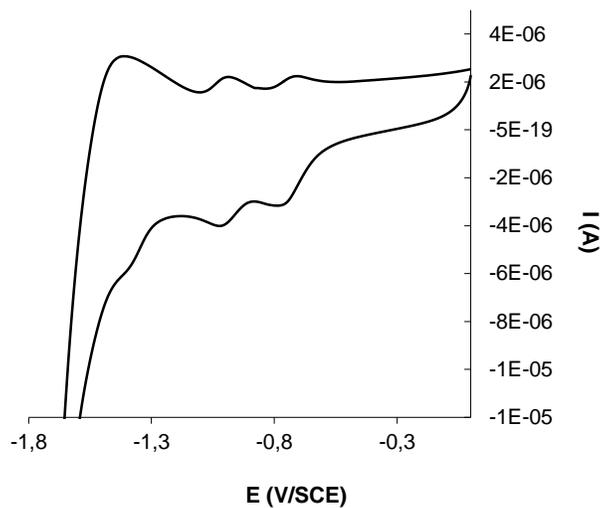
**Figure S53.** Cathodic cyclic voltammetry of  $[\text{Ru}(\text{TAP})_2\text{pytz}'(\text{diN}_3\text{C6})]^{2+}(\text{NO}_3^-)_2$  **24** ( $1 \cdot 10^{-3}$  M) in dry deoxygenated MeCN, V versus SCE at room temperature, 0.1V/s, with 0.1M  $\text{Bu}_4\text{N}^+\text{PF}_6^-$  as supporting electrolyte and a Pt working electrode.



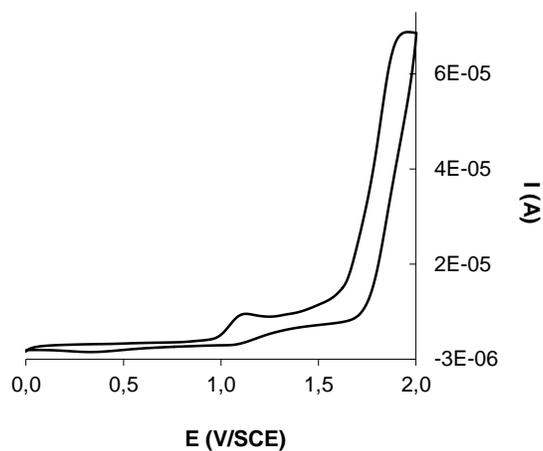
**Figure S54.** Cathodic cyclic voltammetry of  $[\text{Ru}(\text{TAP})_2\text{pytz}'\text{C6}]^{2+}(\text{NO}_3^-)_2$  **19** ( $1 \cdot 10^{-3}$  M) in dry deoxygenated MeCN, V versus SCE at room temperature, 0.1V/s, with 0.1M  $\text{Bu}_4\text{N}^+\text{PF}_6^-$  as supporting electrolyte and a Pt working electrode.



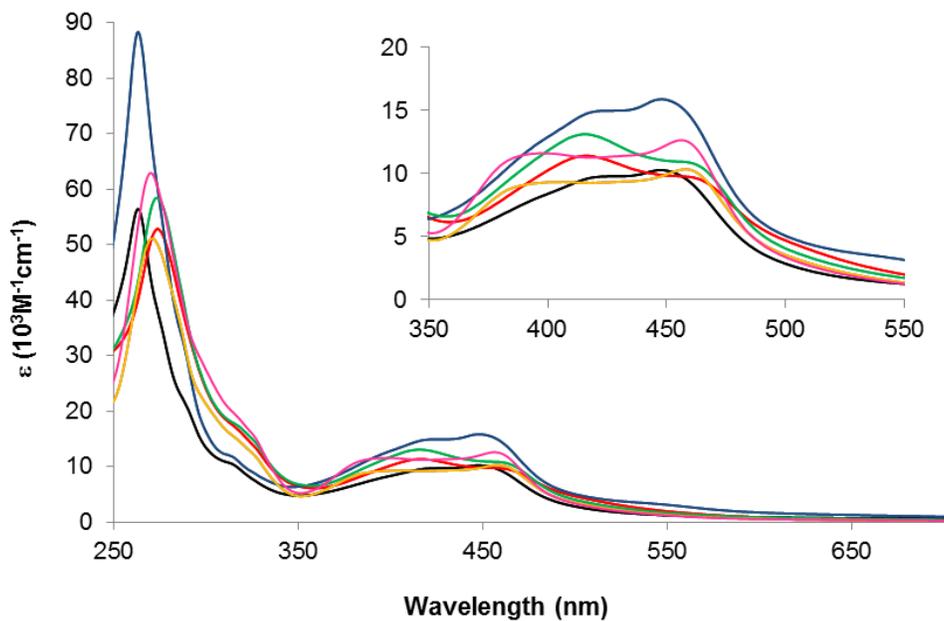
**Figure S55.** Cathodic cyclic voltammetry of  $[\text{Ru}(\text{TAP})_2\text{phen}'(\text{C6})]^{2+}(\text{NO}_3^-)_2$  **14** ( $1.10^{-3}$  M) in dry deoxygenated MeCN, V versus SCE at room temperature, 0.1V/s, with 0.1M  $\text{Bu}_4\text{N}^+\text{PF}_6^-$  as supporting electrolyte and a Pt working electrode.



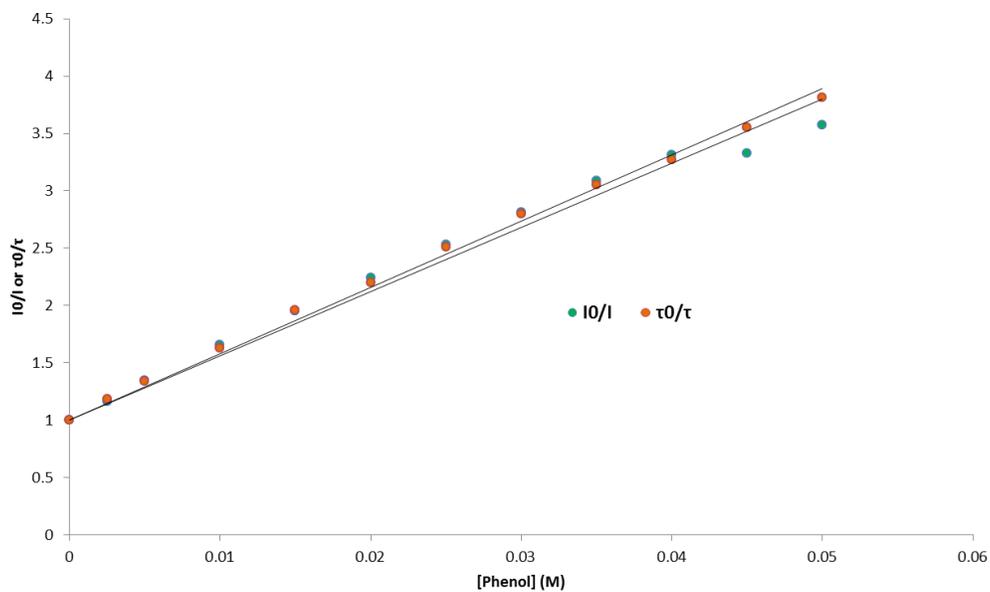
**Figure S56.** Anodic cyclic voltammetry of  $[\text{Ru}(\text{TAP})_2\text{pytz}'(\text{diN}_3\text{C6})]^{2+}(\text{NO}_3^-)_2$  **24** ( $1.10^{-3}$  M) in dry deoxygenated MeCN, V versus SCE at room temperature, 0.1V/s, with 0.1M  $\text{Bu}_4\text{N}^+\text{PF}_6^-$  as supporting electrolyte and a Pt working electrode.



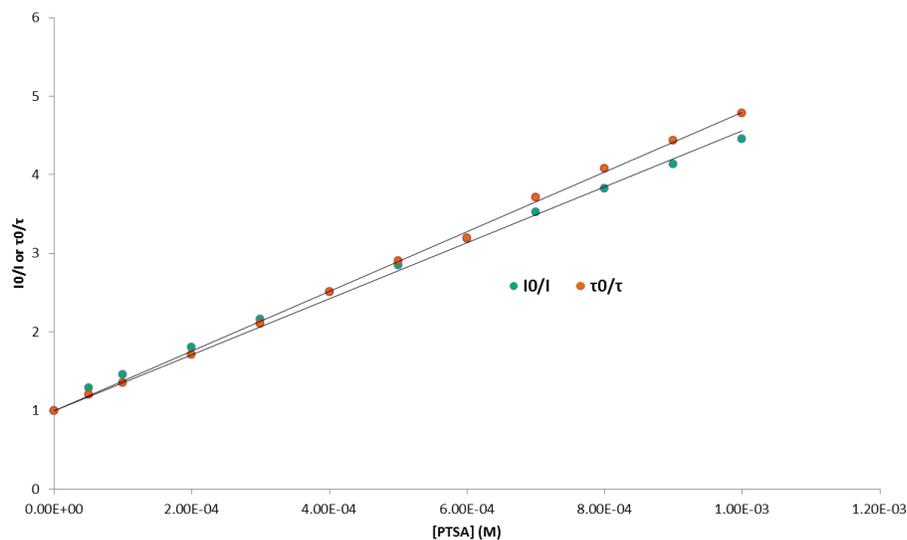
**Figure S57.** Absorption spectra (298 K, air) in MeCN for complexes **6** (black), **7** (red), **13** (blue), **14** (green), **19** (orange) and **24** (pink).



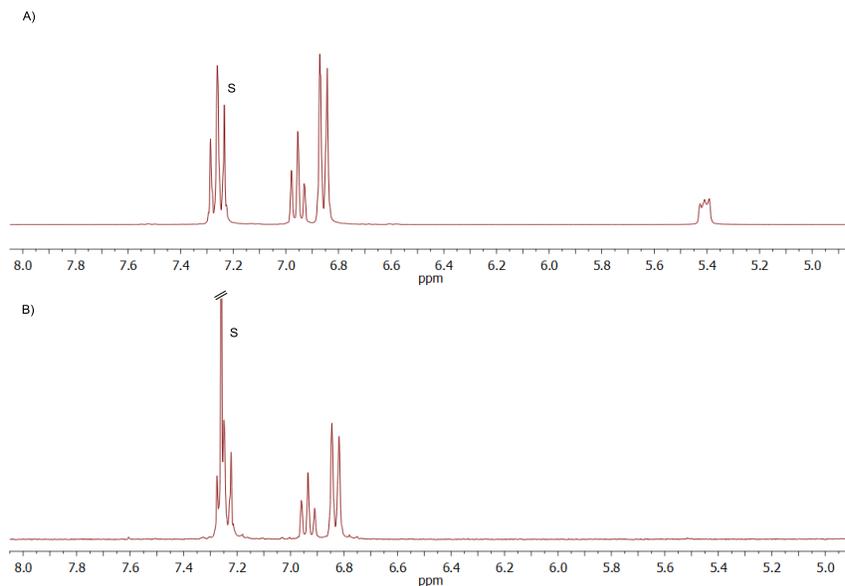
**Figure S58.** Stern-Volmer experiments (luminescence intensities (green) and lifetimes (red)) for  $[\text{Ru}(\text{TAP})_2\text{phen}]^{2+}$  **25** ( $1.10^{-5}$  M) in acetonitrile, in presence of phenol.



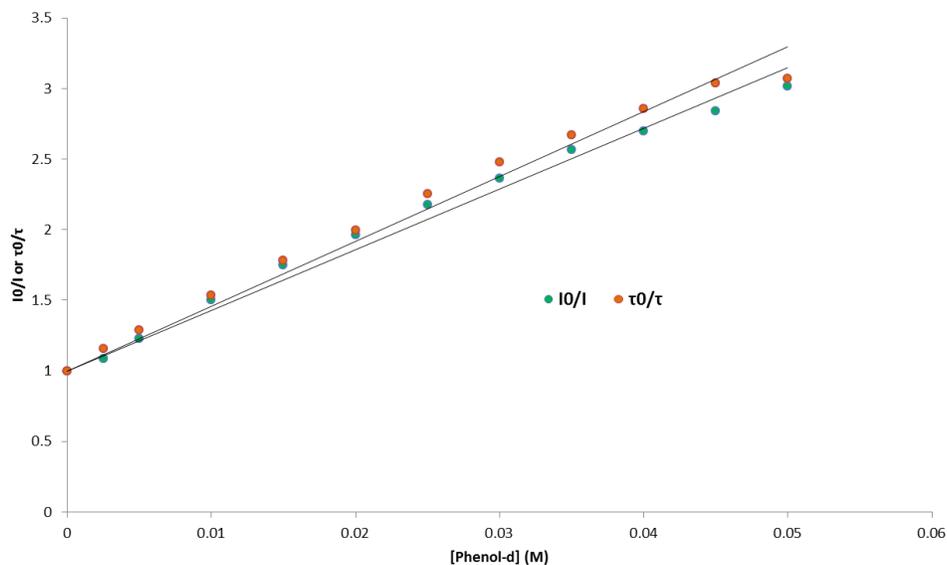
**Figure S59.** Stern-Volmer experiments (luminescence intensities (green) and lifetimes (red)) for  $[\text{Ru}(\text{TAP})_2\text{phen}]^{2+}$  **25** ( $1.10^{-5}$  M) in acetonitrile, in presence of an acid (paratoluene sulfonic acid = PTSA).



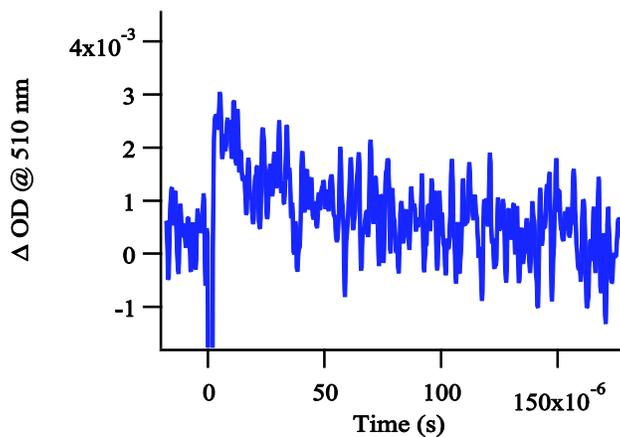
**Figure S60.** Deuterated phenol was obtained after 30 minutes mixing in hot  $\text{CD}_3\text{OD}$ . Deuteration of the phenol moiety was checked by  $^1\text{H}$  NMR (300 MHz, 298 K) in  $\text{CDCl}_3$ , A)  $^1\text{H}$  NMR spectrum of phenol and B)  $^1\text{H}$  NMR of deuterated phenol.



**Figure S61.** Stern-Volmer experiments (luminescence intensities (green) and lifetimes (red)) for  $[\text{Ru}(\text{TAP})_2\text{phen}]^{2+}$  **25** ( $1.10^{-5}$  M) in acetonitrile, in presence of deuterated phenol.



**Figure S62.**  $[\text{Ru}(\text{phen})_2\text{phen}'(\text{C6})]^{2+}(\text{NO}_3^-)_2$  **13** in acetonitrile under inert atmosphere. Decay of the TA at 510 nm in a microseconds timescale.



**Figure S63.** Equation for  $\Delta G_{PCET}^0$  in the case of a PCET: (1.1) ET followed by a HT or (1.2) ET and HT concerted. The following equations cannot be applied in our case due to problems for determinations of important experimental values such as: precise  $E_{red}^*$ , pKa in MeCN, pKa of the reduced and excited complex.

$$\Delta G_{PCET}^0 = -nF \left[ E_{red(Ru^{II}/Ru^I)}^* - E_{ox(phOH/phOH^{*\cdot+})} \right] + 0.0059 \times \{pK_a(phOH^{*\cdot+}) - pK_a(Ru^I)\} \quad (1.1)$$

$$\Delta G_{PCET}^0 = -nF \left[ E_{red(Ru^{II}/Ru^I)}^* - E_{ox(phOH/phOH^{*\cdot+})} \right] + 0.0059 \times \{pK_a(phOH^{*\cdot+}) - pK_a(Ru^{*II})\} \quad (1.2)$$

(1) Gans, P. Data Fitting in the Chemical Sciences: By the Method of Least Squares; John Wiley & Sons, 1992.