SUPLEMENTARY INFORMATION

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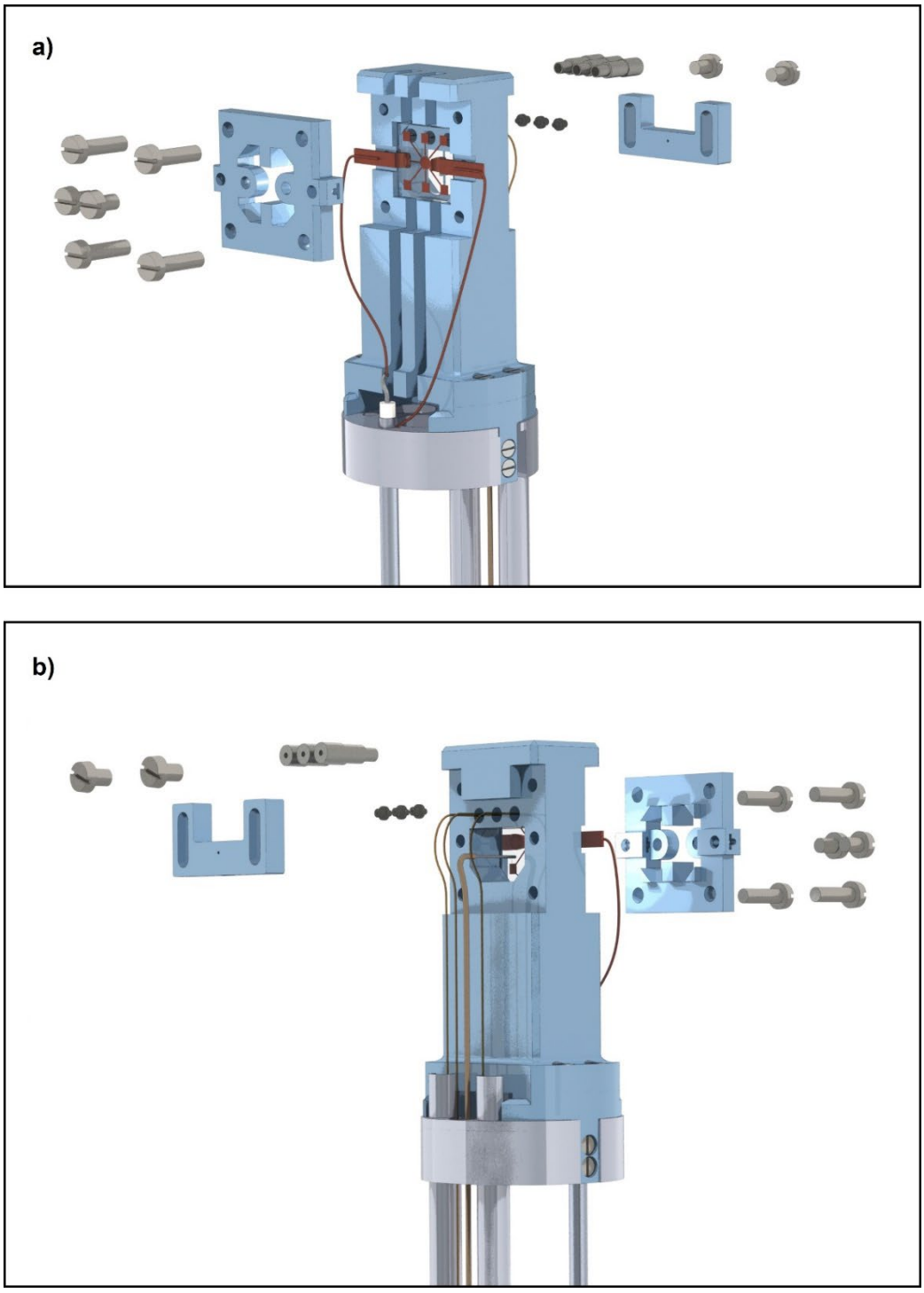

Scheme S1. Detailed view of the front and back side of the microfluidic chip integrated in the 3D printed-holder. **A**) Top Clamp, with screws for mounting the Top Clamp and for pressing the copper contact strips onto the NMR chip. The contact strips are still in place on the main holder. On the backside the three microfluidic ferrules and fiber slider holder can be seen. **B**) Backside of the same exploded view, where the three capillaries can be seen entering the threaded ferrule holes, as well as the optical fiber pointed towards the chip.

Suplementary Table 1. Experimental data for the study of the photo-CIDNP efficiency as a function of p-fluorophenol / FMN. Experimental data obtained for Figure 2d. Syringe in pump 1 contained 10 mM of *p*-fluorophenol and 300 mM of TFE. Syringe in pump 2 contained 10 mM of *p*-fluorophenol, 300 mM of TFE, 600 mM of TFP and 5 mM of FMN.

Pump 1 Flow rate	**Pump 2 Flow rate**	**[TFP]**	**[FMN]**	**[p-fluorophenol] / [FMN]**	**Integral fluorophenol**
2,0	0	--	--	--	--
1,80	0,2	62	0,43	23,2	67
1,80	0,2	61	0,42	23,6	71
1,75	0,25	78	0,54	18,5	82
1,70	0,3	81	0,56	17,7	83
1,70	0,3	87	0,60	16,5	87
1,70	0,3	96	0,66	15,0	93
1,65	0,35	111	0,77	12,9	96
1,65	0,35	116	0,80	12,4	81
1,65	0,35	137	0,95	10,5	85
1,60	0,4	120	0,83	23	82
1,50	0,5	140	0,97	10,3	73
1,40	0,6	191	1,33	7,5	73
1,30	0,7	209	1,45	6,9	81
1,20	0,8	250	1,74	5,8	64
1,1	0,9	323	2,24	4,5	70
1	1	346	2,40	4,2	76
0,75	1,25	405	2,81	3,5	67
0,5	1,5	485	3,37	3,0	52
0,25	1,75	528	3,67	2,7	57
0	2	655	4,55	2,2	58
0	2	720	5	2,0	71
0	2	735	5,1	2,0	66

Suplementary Table 2. **Acquisition parameters for the multinuclear multidimensional NMR experiments:** Acquisition parameters for the NMR experiments shown in Figures 3, 4 and 5. Sw and sw1 are the spectral windows in the direct and indirect detection, respectively.

Sample	Experiment	Number of increments in indirect detection	Number of scans per increment	sw	sw1
Trifluoroethanol	$^{19}F^{1}H$-HMQC	128	4	56298	6999
Trifluoroethanol (Figure 4 A)	$\{^{1}H\}^{19}F^{13}C$-HMBC	256	64	56298	31446
Trifluoroethanol (Figure 4 B)	$^{19}F^{13}C$-HMBC	256	64	56298	31446
Trifluoroethanol (Figure 4 C)	$\{^{1}H\}^{19}F^{13}C$-HMQC	64	128	14000	11999
Trifluoroethanol (Figure 4 D)	$^{19}F^{13}C$-HMQC	64	128	14000	11999
13 mM p-fluorophenol, 1.1 mM FMN, 300mM TFE (Figure 5 D)	2D Photo-CIDNP $\{1H\}^{19}F$-^{1}H HMQC	16	16	49200	16000
0.57 mM p-fluorophenol, 13.2 mM TFE (Figure 5 E)	$\{1H\}^{19}F$-^{1}H HMQC	16	16	113636	10003

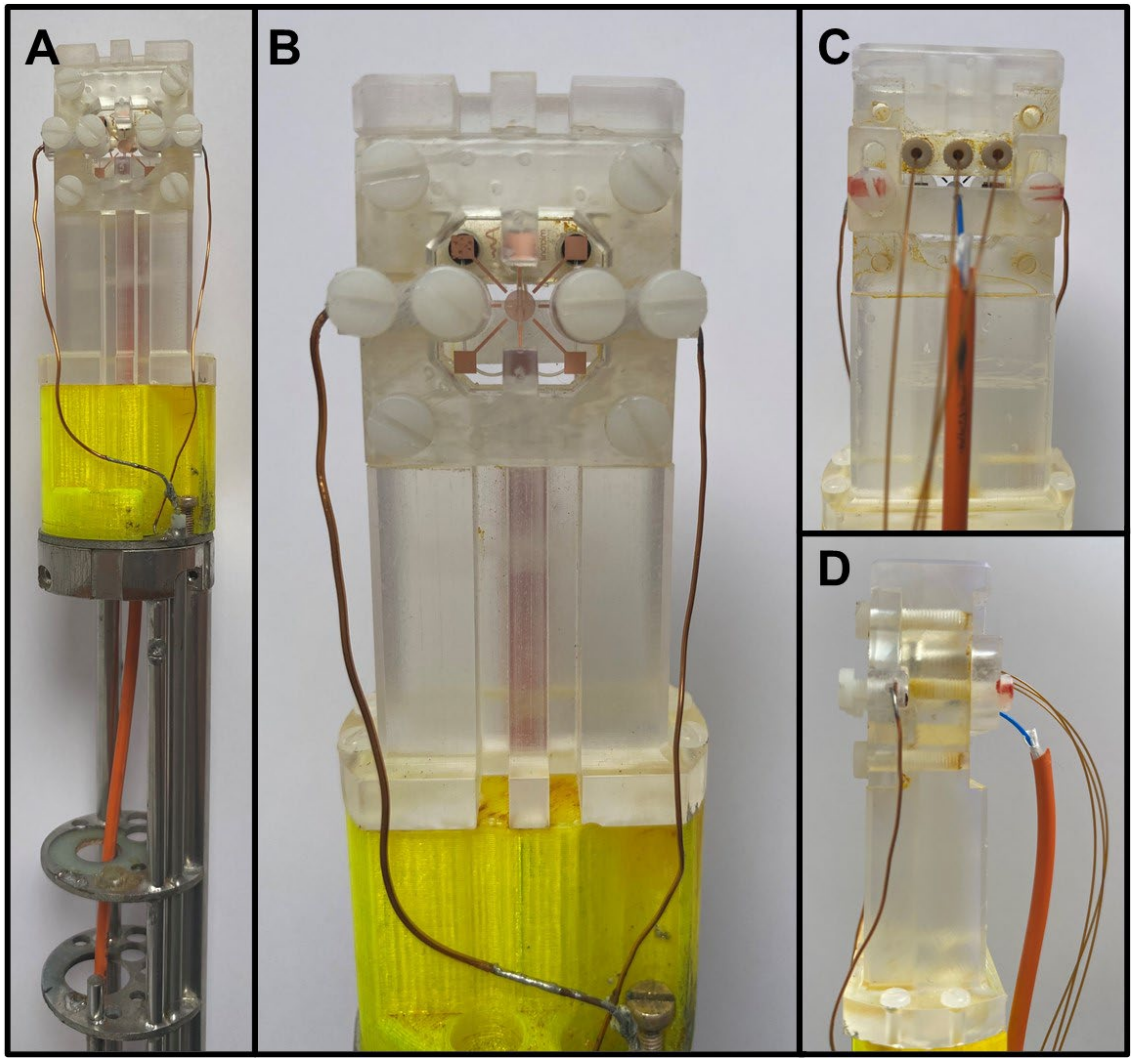

Figure S1. Photographs of the microfluidic chip integrated in the 3D printed-holder. A) Front view that visualizes the decommissioned, non-functional probe that was used as a probe platform. **B**) Zoom of the front view of the chip-holder showing the planar spiral coil integrated on top of the microfluidic chip and the electronic connections. **C)** Back side of the chip-holder showing the fused silica capillaries for the microfluidic connections and the optical fiber to illuminate the NMR active volume. **D)** Cross-section view of the chip-holder showing one electronic connection, the fused silica capillaries for the microfluidic connections and the optical fiber to illuminate the NMR active volume.

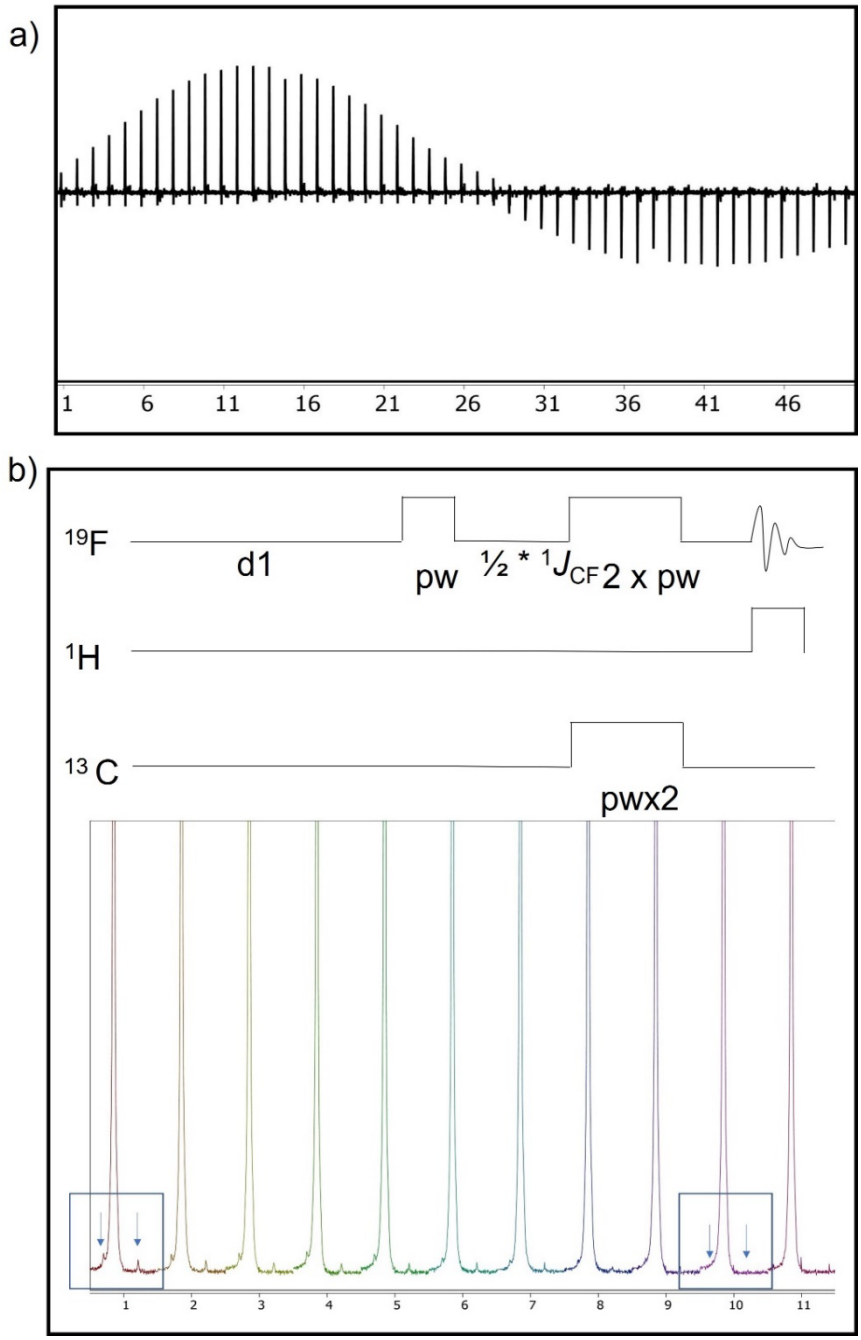

Figure S2. Calibration of the ^{19}F 90^{o} pulse width on neat TFE in a hardware configuration with two combiners (Scheme 2e, main text) that allows the excitation of up to three different nuclides. (a): 90^{o} pulse width calibration for ^{19}F with an experiment acquired in the arrayed mode (50 steps, starting from 0, increments of 1). The first null of the ^{19}F signal corresponds to the 180^{o} pulse width for ^{19}F (pw_{180}=29). The acquisition parameters are the following: preacquisition delay= 3, acquisition time= 0.5 and number of scans= 2. **(b):** 90^{o} pulse width calibration for ^{13}C with an experiment acquired in the arrayed mode (11 steps, starting from 0, increments of 15). The first null for the ^{13}C satellite peaks of the TFE ^{19}F signal (step=10) corresponds to the 90^{o} pulse width for ^{13}C (pwx= 135). The experiment was run with ^{1}H decoupling. The acquisition parameters are the following: $^{1}J_{CF}$ = 290 Hz, decoupling power=40, ^{19}F pulse width= 14.5, preacquisition delay= 3, acquisition time= 0.5 and number of scans= 64.

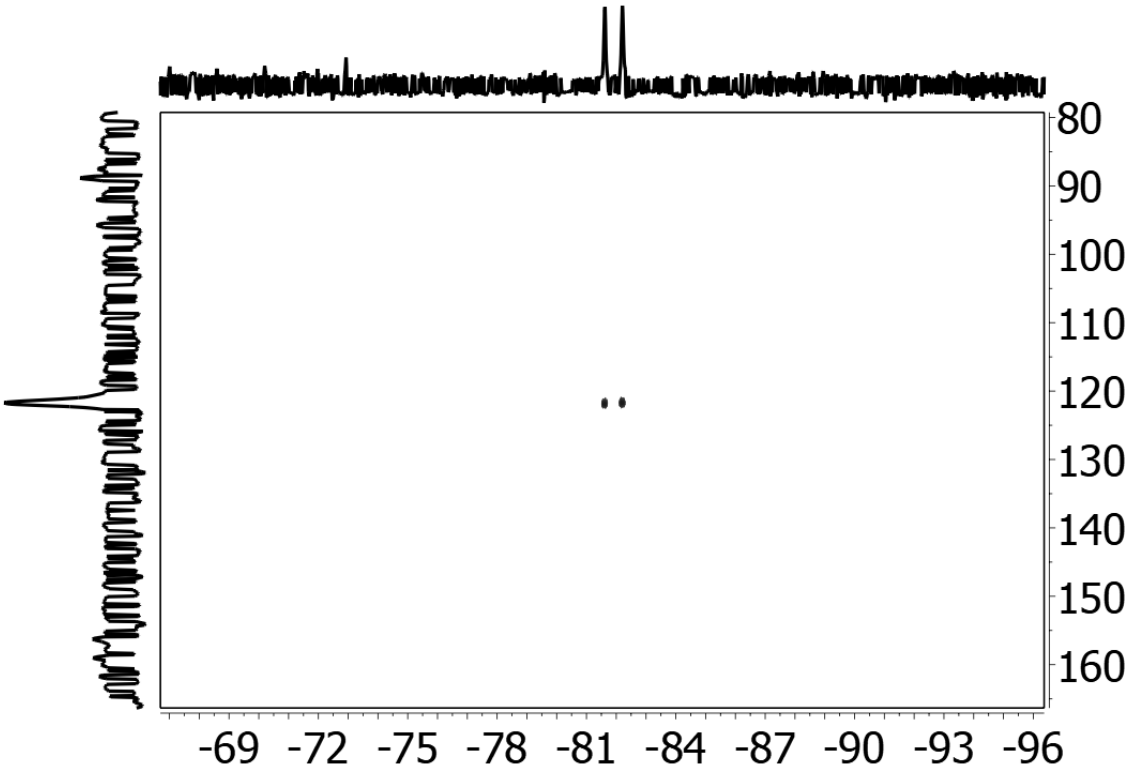

Figure S3. ^{19}F-^{13}C HMQC on neat TFE from the multinuclear multidimensional NMR experiments on the broadband spiral planar microcoil shown in Figure 4, main text.

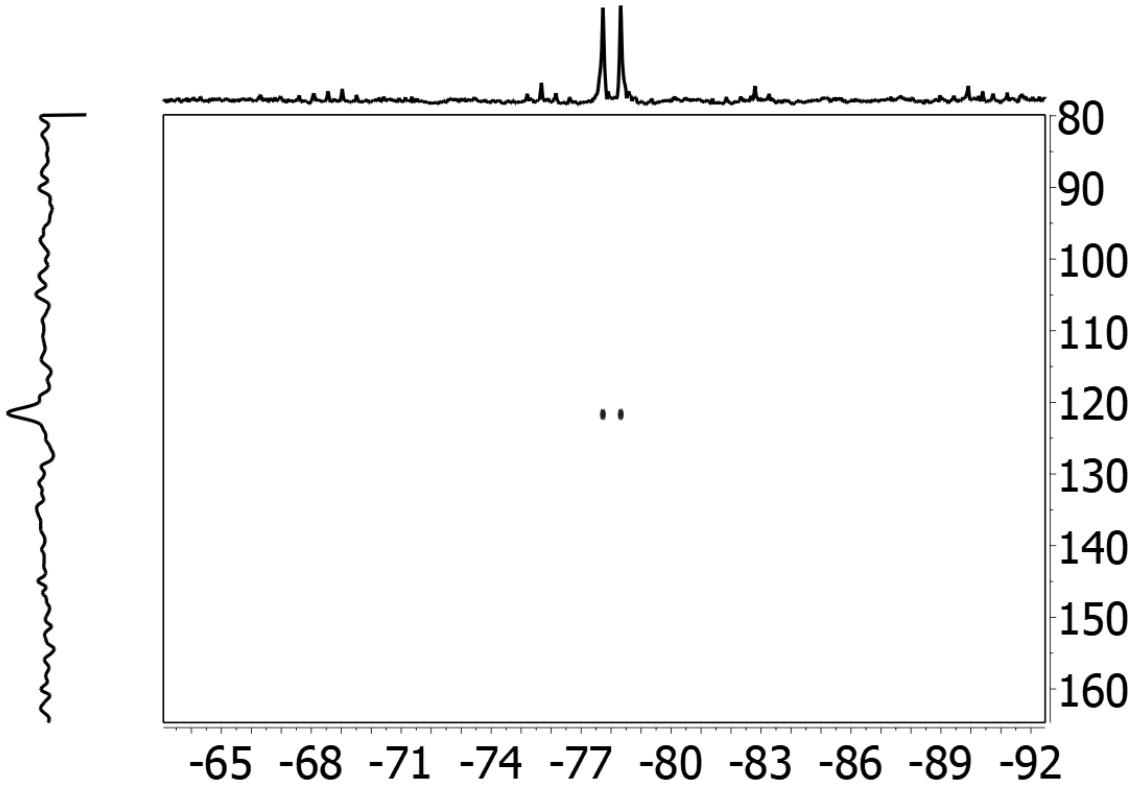

Figure S4. ^{19}F-^{13}C HMQC on neat TFE with ^{1}H decoupled mode from the multinuclear multidimensional NMR experiments on the broadband spiral planar microcoil shown in Figure 4, main text.

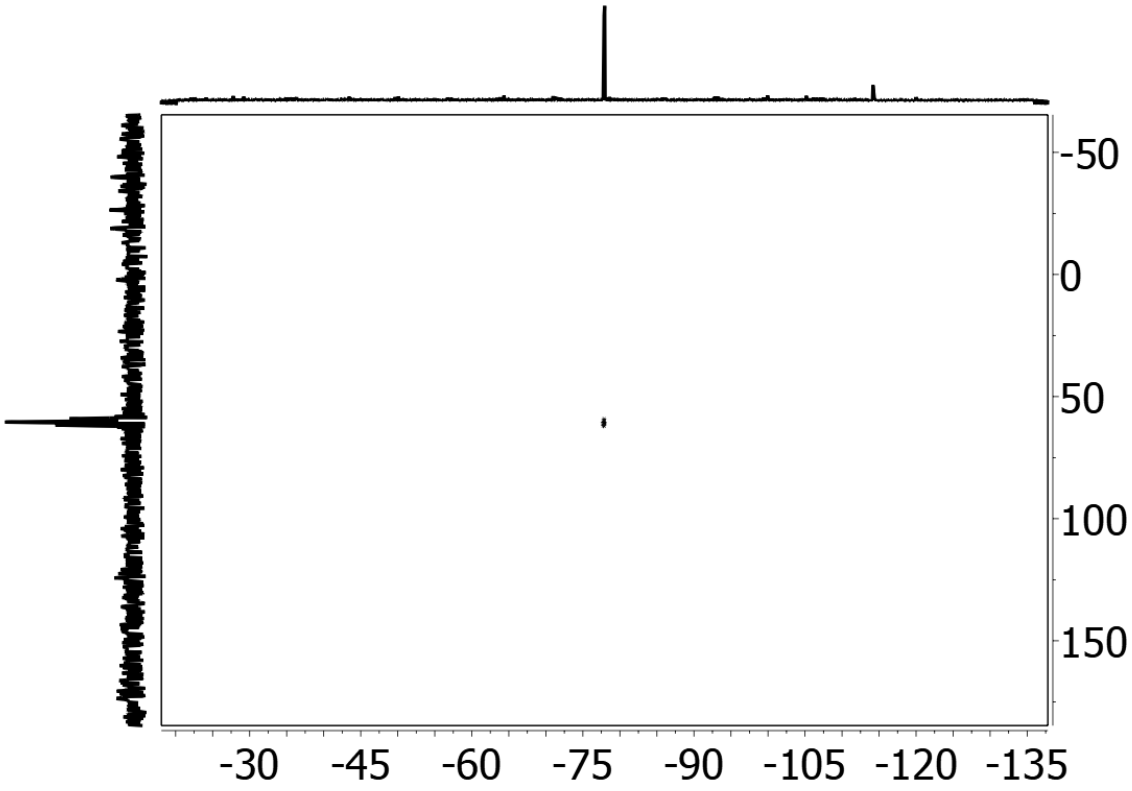

Figure S5. $^{19}F^{13}C$-HMBC on neat TFE from the multinuclear multidimensional NMR experiments on the broadband spiral planar microcoil shown in Figure 4, main text.

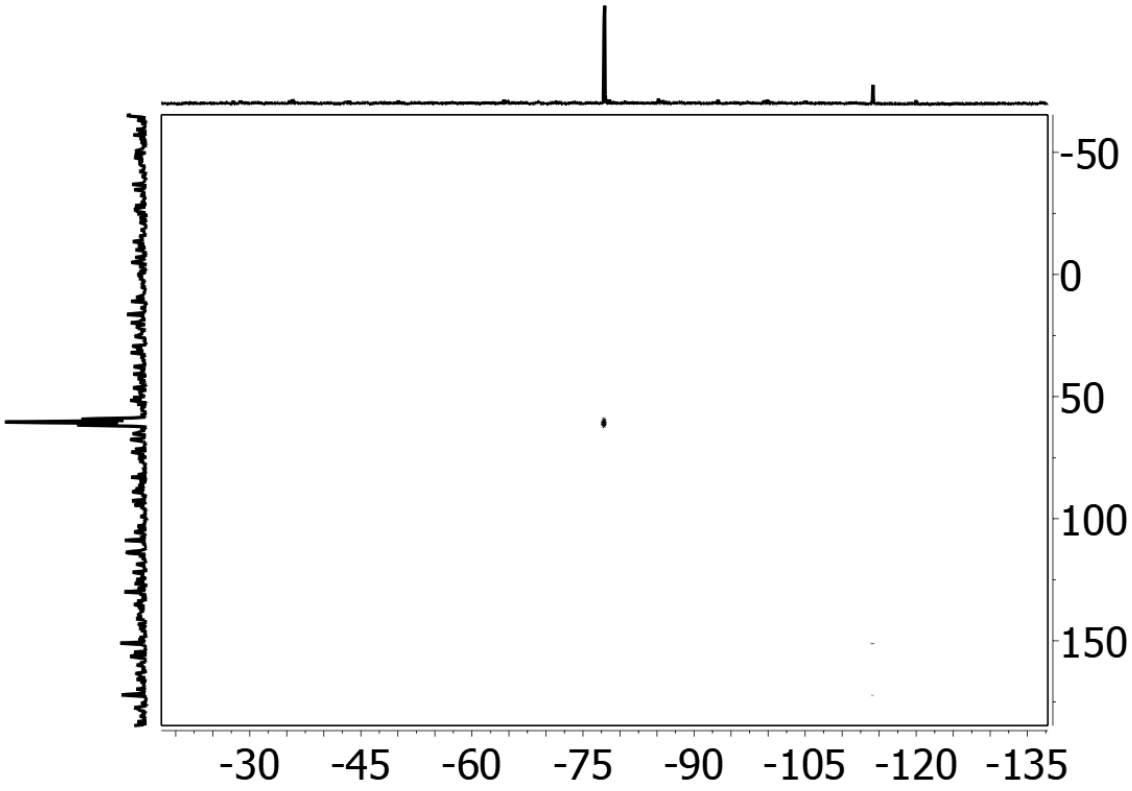

Figure S6. ^{19}F-^{13}C HMBC on neat TFE with ^{1}H decoupled mode from the multinuclear multidimensional NMR experiments on the broadband spiral planar microcoil from Figure 4, main text.

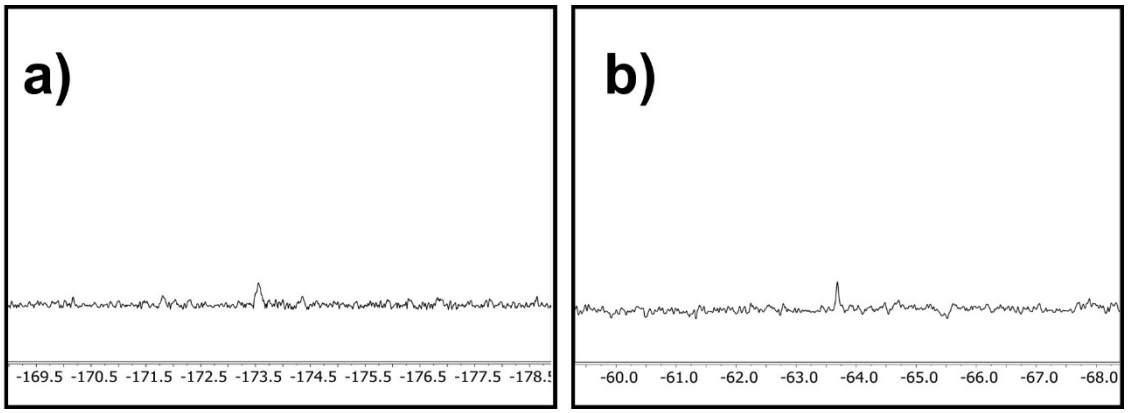

Figure S7. Comparison of required NMR experimental time for a certain SNR between a photo-CIDNP-assisted broad-band non-resonance planar coil (this work) and a broad-band non-resonance planar coil from our previous work.[1] A): ^{19}F NMR photo-CIDNP spectrum of 80 picomole of 5-fluorouracile (3.2 mM of 5-fluorouracile and 0.2 mM of FMN) in stopped flow (SNR= 5.3 measured with the MestRenova script). The number of scans is 100 and the NMR experiment time is 1 min 41 seconds. Line broadening is 10. **B)**: ^{19}F-NMR spectra of 25 picomole of trifluoromethylphenol from our previous work (SNR = 6,0 measured with the MestRenova script).[1] The number of scans is 16000 and the NMR experiment time is 6h 43 min. Line broadening is 10.

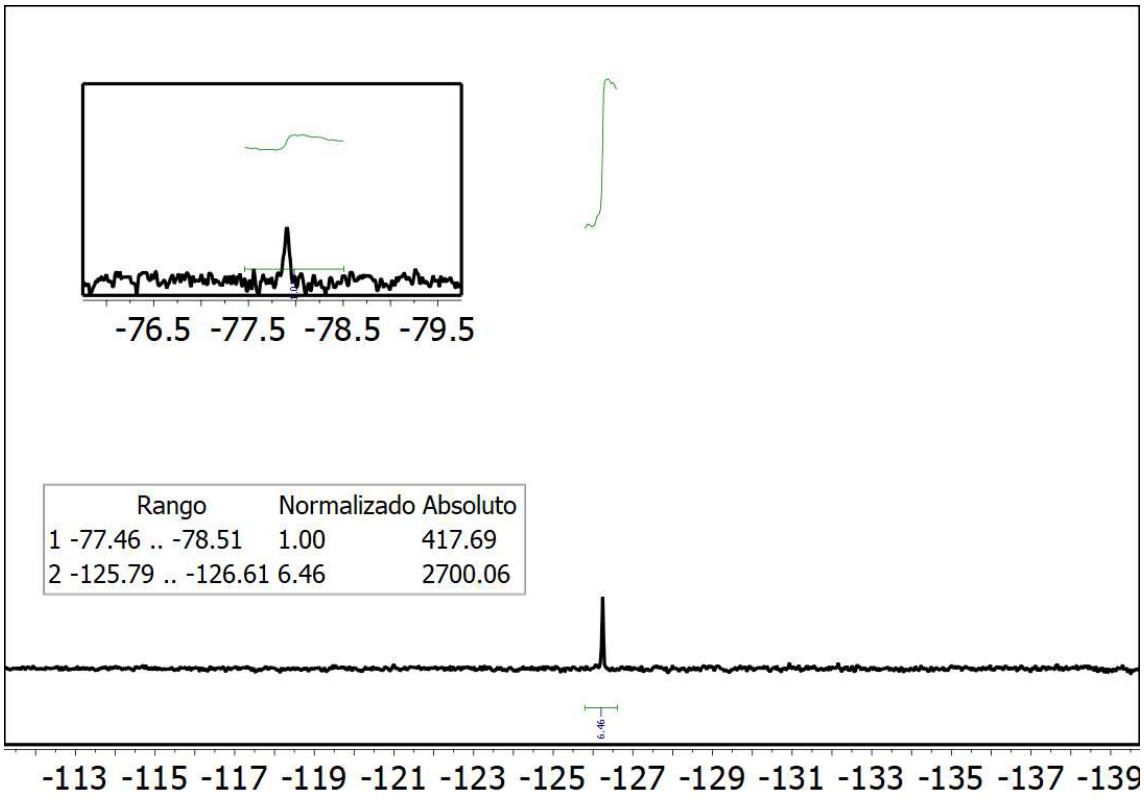

Figure S8. Photo-CIDNP 19F NMR for the calculation of the signal enhancement. NMR spectrum of 13mM of *p*-fluorophenol and 1.1. mM of TFE in the presence of 300 mM of TFE. The integral of TFE has been normalized to 1, resulting in an integral value for the *p*-fluorophenol of 6.46, which corresponds to a signal enhancement of roughly 450 times. The number of scans is 256.

REFERENCES

1. Fratila, R. M., Victoria Gomez, M., Sykora, S. & Velders, A. H. Multinuclear nanoliter one-dimensional and two-dimensional NMR spectroscopy with a single non-resonant microcoil. *Nat. Commun.* **5**, 3025 (2014).