1. General

All solvents and reagents were of analytical grade and used directly without further purification. 5% Pd/C and 5% Pd/$BaSO_4$ catalysts used in this study were purchased from Sigma-Aldrich, while D_2O (>99.9%) was from Merck; HPLC-grade solvents from VWR were used without purification. The propylene carbonate was bought from Acros Organics. The cartridge containing 5% Pd/polymer-based spherical activated carbon (PBSAC) was filled in-house.

2. General aspects of the CF deuteration

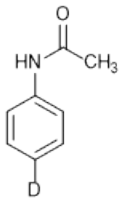
The CF deuteration reactions were carried out in an H-Cube® reactor (ThalesNano Inc.) with D_2O as deuterium source. The catalyst cartridge (with internal dimensions of 30×4 mm) was filled with ca. 100 mg of the heterogeneous hydrogenation catalyst. It was then placed into a thermostat unit controlled by a Peltier system, up to a maximum of 100 °C. The pressure of the system was set by a backpressure regulator to a maximum of 100 bar, and the CF of the solution of the starting material was provided by an HPLC pump (Knauer WellChrom K-120). For the CF reactions, 3 mg mL^{-1} solution of the appropriate starting material was prepared in propylene cabonate. The solution was homogenized by sonication for 5 min and then pumped through the CF reactor under the set conditions. A single run was carried out with 100 mg starting material. After the completion of the reaction, the reaction mixture was collected, diluted with water, freeze and lyophilized.

3. Product analysis

The products obtained were characterized by NMR spectroscopy. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer, in DMSO-d_6 as solvent, at 400.1 MHz. Chemical shifts are expressed in δ and are internally referenced (^{1}H NMR: δ 2.50 in DMSO-d_6). Conversion and deuterium incorporation values were determined via the ^{1}H-NMR spectra of the crude materials. Deuterium contents were determined from the relative intensities of the ^{1}H-NMR indicator signals. Elemental analyses were performed with a Perkin–Elmer CHNS-2400Ser II Elemental Analyzer.

4. Characterization of products

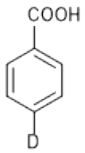
N-(phenyl-4-^{2}H)acetamide (**2**)



White crystals; m.p. 110.2-111.8 °C (data is in agreement with the literature reference: 110-112 °C)[1]

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.91 (s, 1H), 7.56 (d, *J*=8.2 Hz, 2H), 7.27 (d, *J*=8.2 Hz, 2H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.3, 139.3, 128.6, 123.0, 118.9, 24.0.

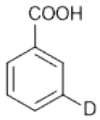
Benzoic-4-^{2}H acid (**4**)



White crystals; m.p. 119.1-121.4 °C (data is in agreement with the literature reference: 119-121 °C)[1]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, *J*=7.5 Hz, 2H), 7.50 (d, *J*=7.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.4, 132.9, 130.8, 129.3, 128.6.

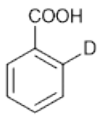
Benzoic-3-^{2}H acid (**6**)



White crystals; m.p. 119.6-121.3 °C (data is in agreement with the literature reference: 121 °C)[2]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91-7.95 (m, 2H), 7.58-7.62 (m, 1H), 7.47 (t, *J*=8.3 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.3, 132.9, 130.7, 129.3, 128.6.

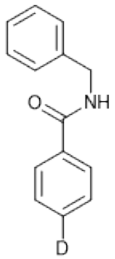
Benzoic-2-^{2}H acid (**8**)



White crystals; m.p. 119.3-121.1 °C (data is in agreement with the literature reference: 121 °C)[2]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, J=7.3, 1H), 7.58-7.65 (m, 1H), 7.47-7.54 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.3, 132.9, 130.6, 129.2, 128.6.

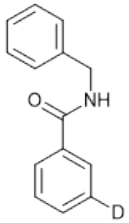
N-benzylbenzamide-4-^{2}H (**10**)



White crystals; m.p. 104.1-106.2 °C (compound is known,[3] but m.p. not published)

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.02 (t, J=5.3, 1H), 7.90 (d, J=7.4, 2H), 7.47 (d, J=7.4, 2H), 7.19-7.28 (m, 1H) 7.28-7.37 (m, 4H), 4.49 (d, J=5.3, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.2, 139.7, 134.3, 130.9, 128.3, 128.2, 127.2, 127.1, 126.7, 42.6.

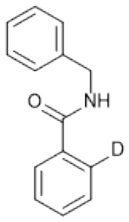
N-benzylbenzamide-3-^{2}H (**12**)



White crystals; m.p. 104.1-106.2 °C

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.04 (t, J=5.3, 1H), 7.87-7.92 (m, 2H), 7.44-7.56 (m, 2H), 7.19-7.28 (m, 1H) 7.28-7.37 (m, 4H), 4.49 (d, J=5.3, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.2, 139.7, 134.3, 131.1, 128.3, 128.2, 128.0, 127.2, 127.1, 127.1, 126.7, 42.6. $C_{14}H_{12}DNO$ (212.11): C, 79.22, H, 6.65, N, 6.60; found C, 79.31, H, 6.61, N, 6.71.

N-benzylbenzamide-2-^{2}H (**14**)



White crystals; m.p. 104.1-106.2 °C

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.05 (t, J=5.3, 1H), 7.88 (d, J=7.4, 1H), 7.43-7.56 (m, 3H), 7.19-7.28 (m, 1H) 7.28-7.37 (m, 4H), 4.48 (d, J=5.3, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ

166.4, 139.8, 134.3, 131.4, 128.5, 128.4, 128.3, 127.3, 127.3, 127.0, 126.9 42.6. $C_{14}H_{12}DNO$ (212.11): C, 79.22, H, 6.65, N, 6.60; found C, 79.29, H, 6.64, N, 6.73.

5. ^{1}H NMR spectra

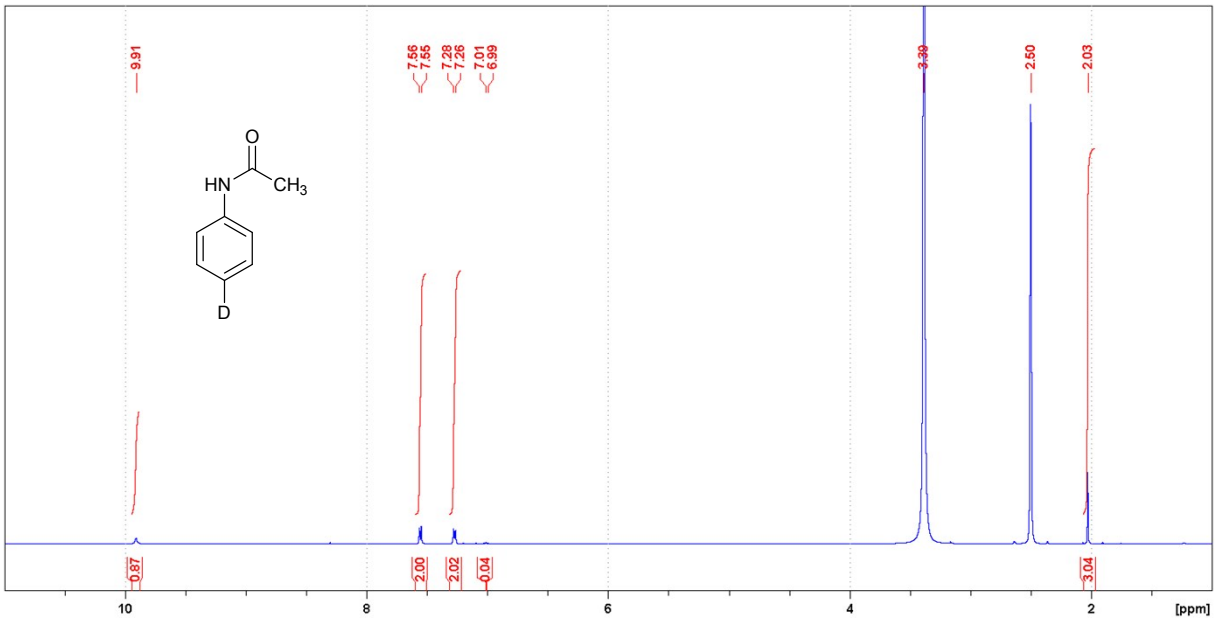


Figure S1. ^{1}H NMR spectrum of **2** measured in DMSO-d_6 at 303 K.

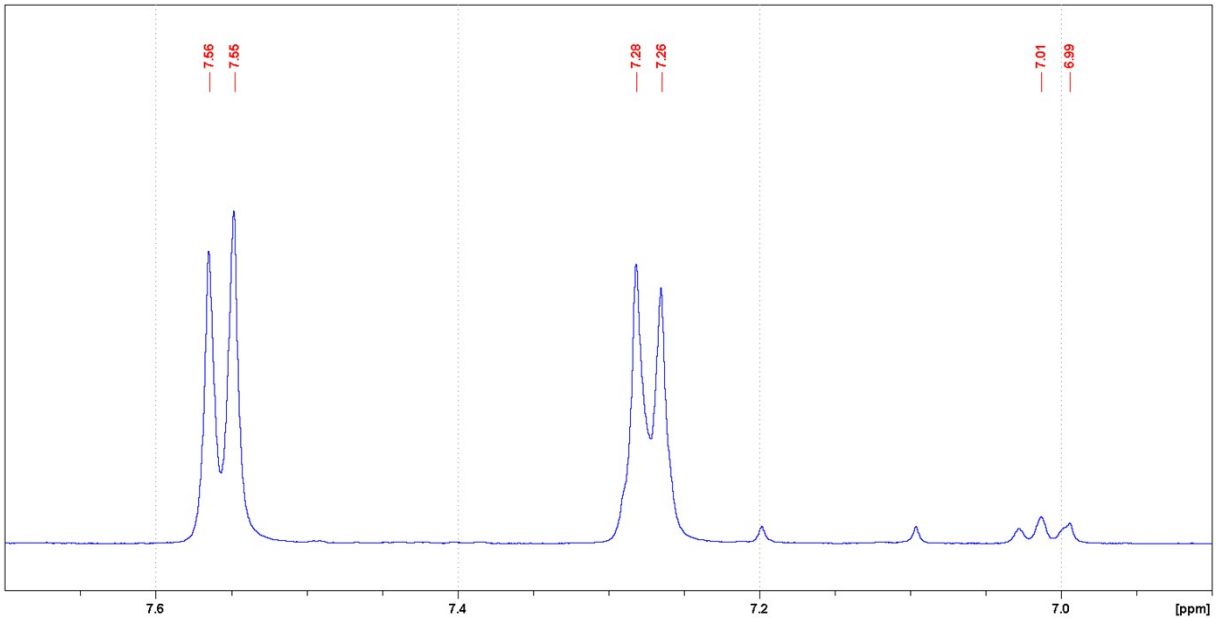


Figure S2. ^{1}H NMR spectrum of **2** measured in DMSO-d_6 at 303 K (aromatic section).

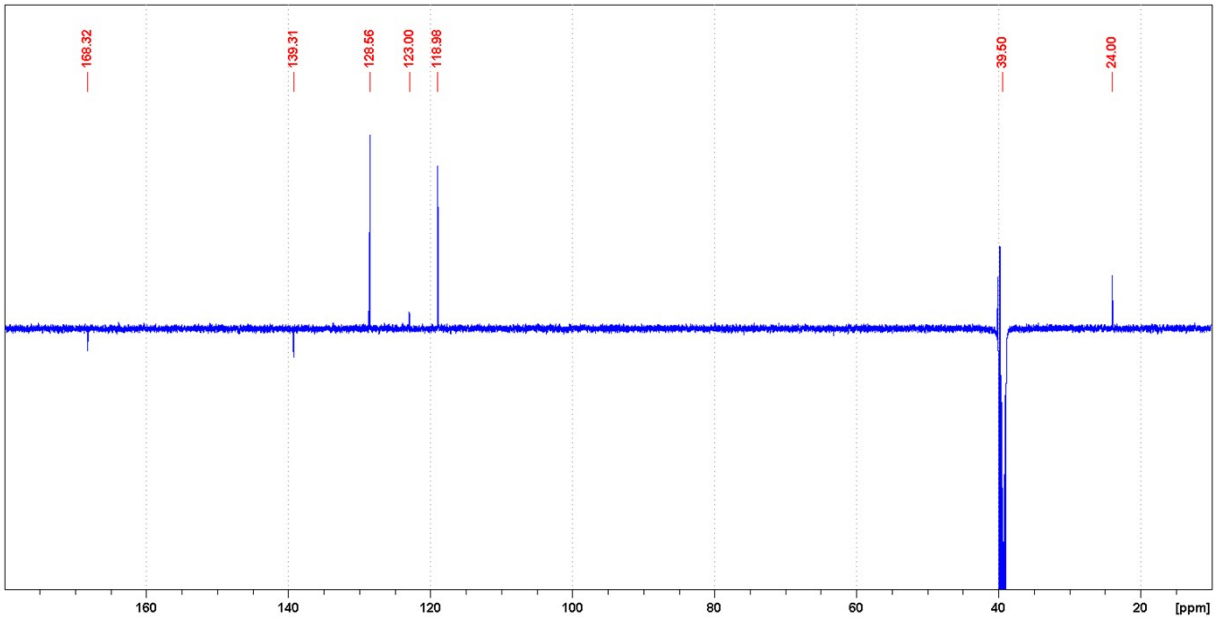


Figure S3. APT NMR spectrum of **2** measured in DMSO-d_6 at 303 K.

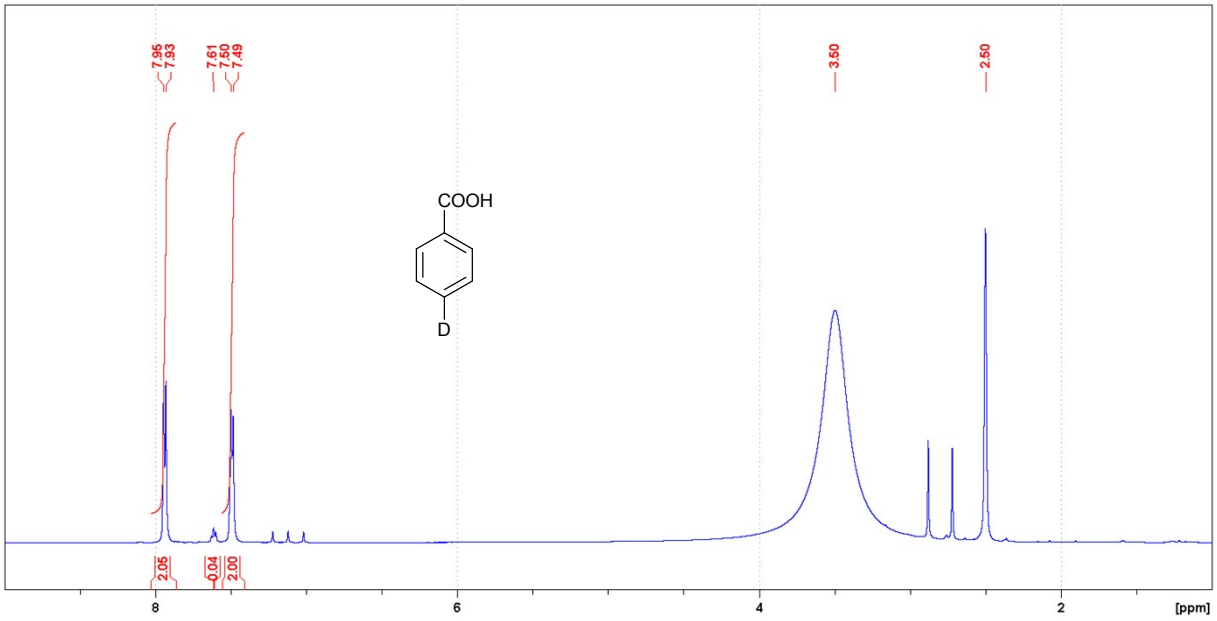


Figure S4. ^{1}H NMR spectrum of **4** measured in DMSO-d_6 at 303 K.

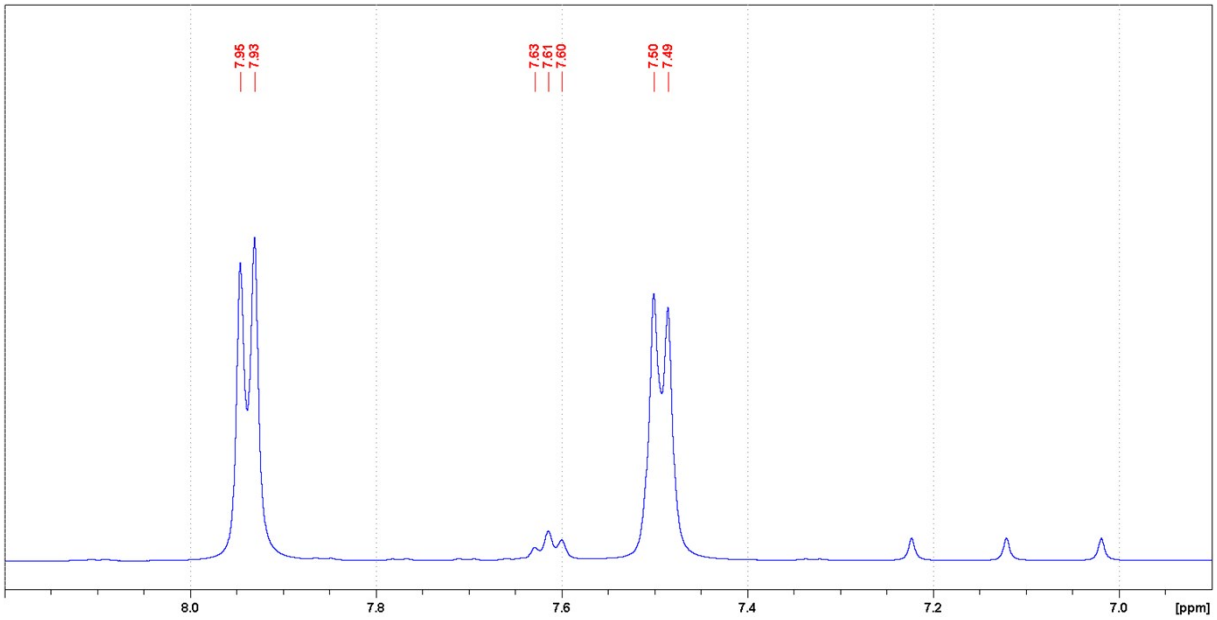


Figure S5. ^{1}H NMR spectrum of **4** measured in DMSO-d_6 at 303 K (aromatic section).

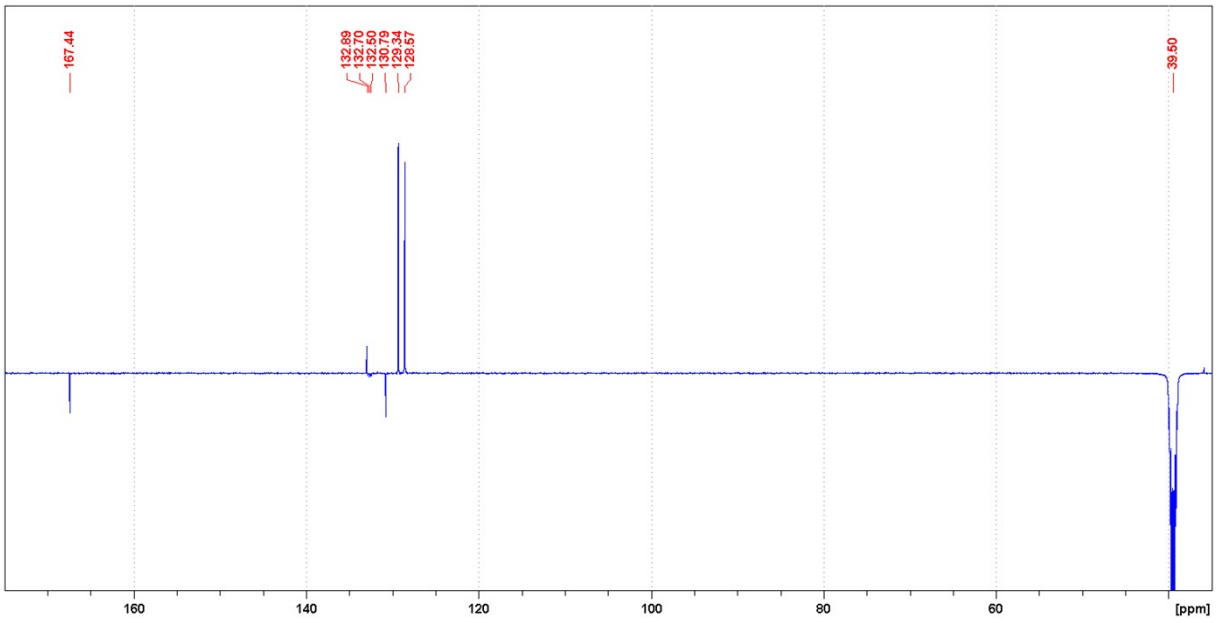


Figure S6. APT NMR spectrum of **4** measured in DMSO-d_6 at 303 K.

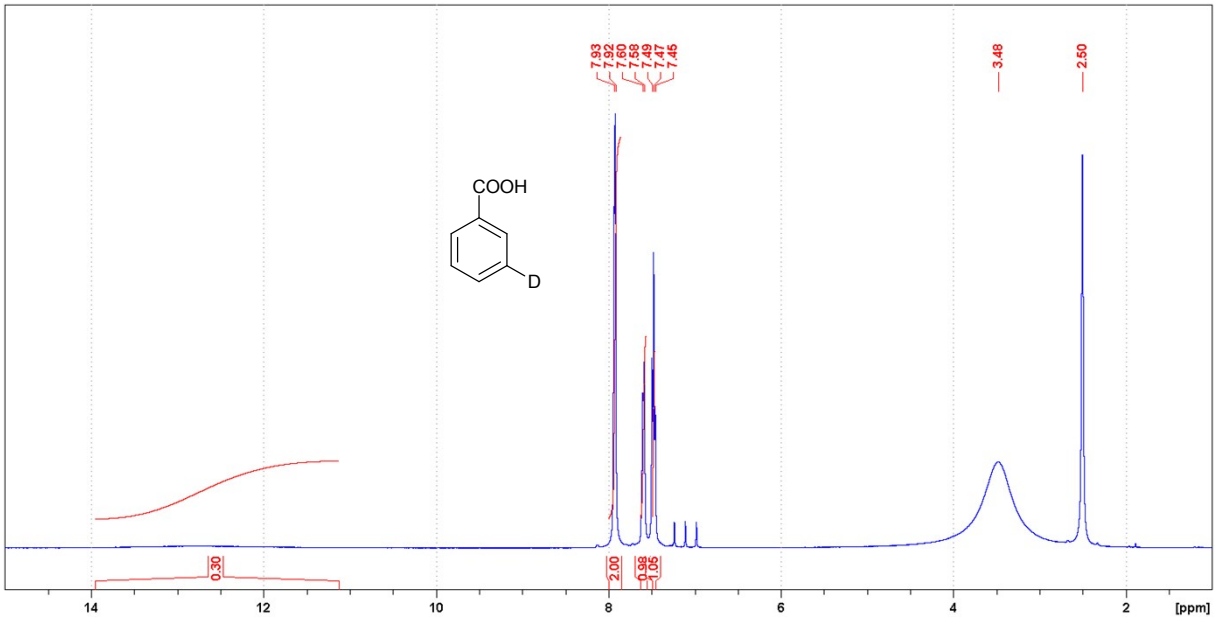


Figure S7. ^{1}H NMR spectrum of **6** measured in DMSO-d_6 at 303 K.

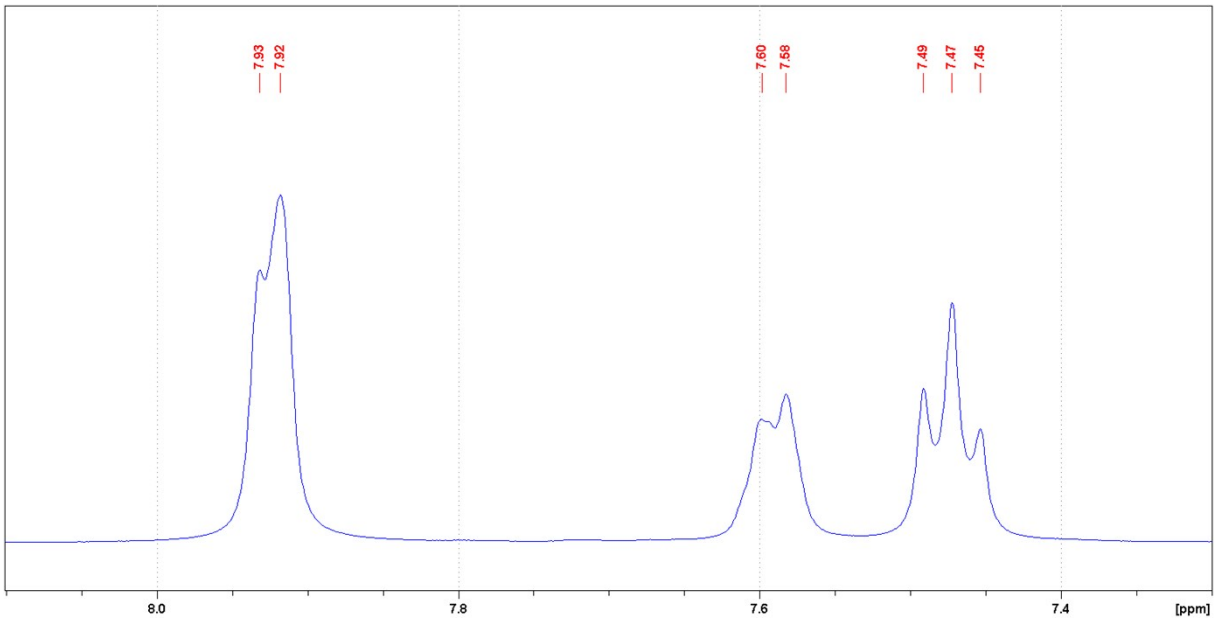


Figure S8. ^{1}H NMR spectrum of **6** measured in DMSO-d_6 at 303 K (aromatic section).

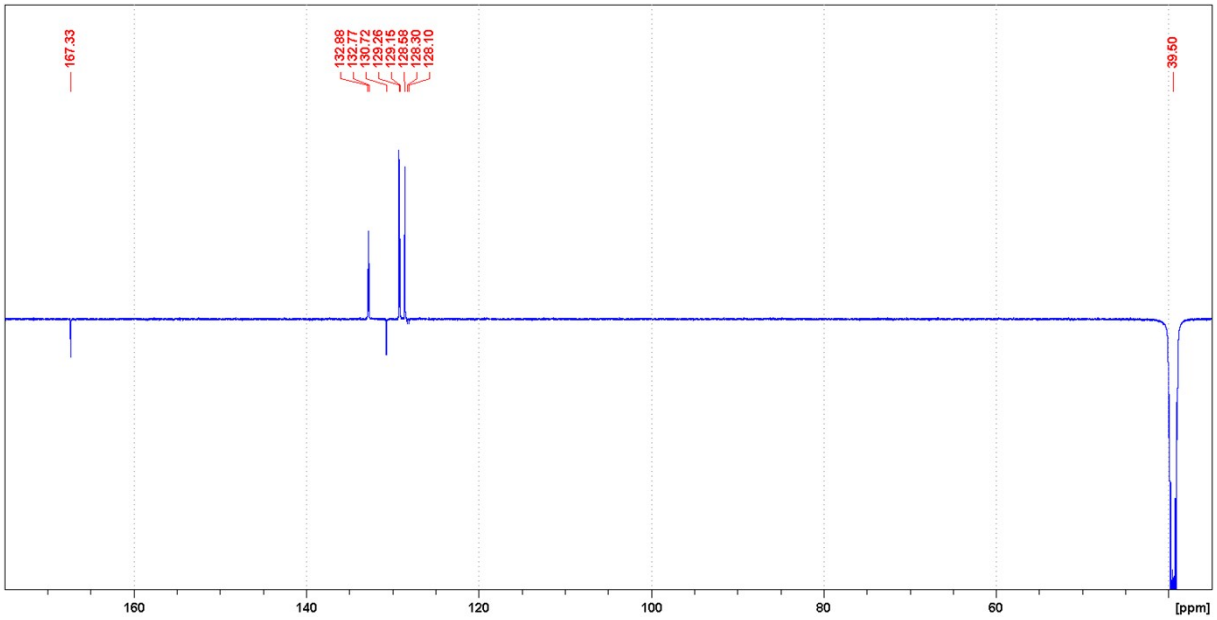


Figure S9. APT NMR spectrum of **6** measured in DMSO-d_6 at 303 K.

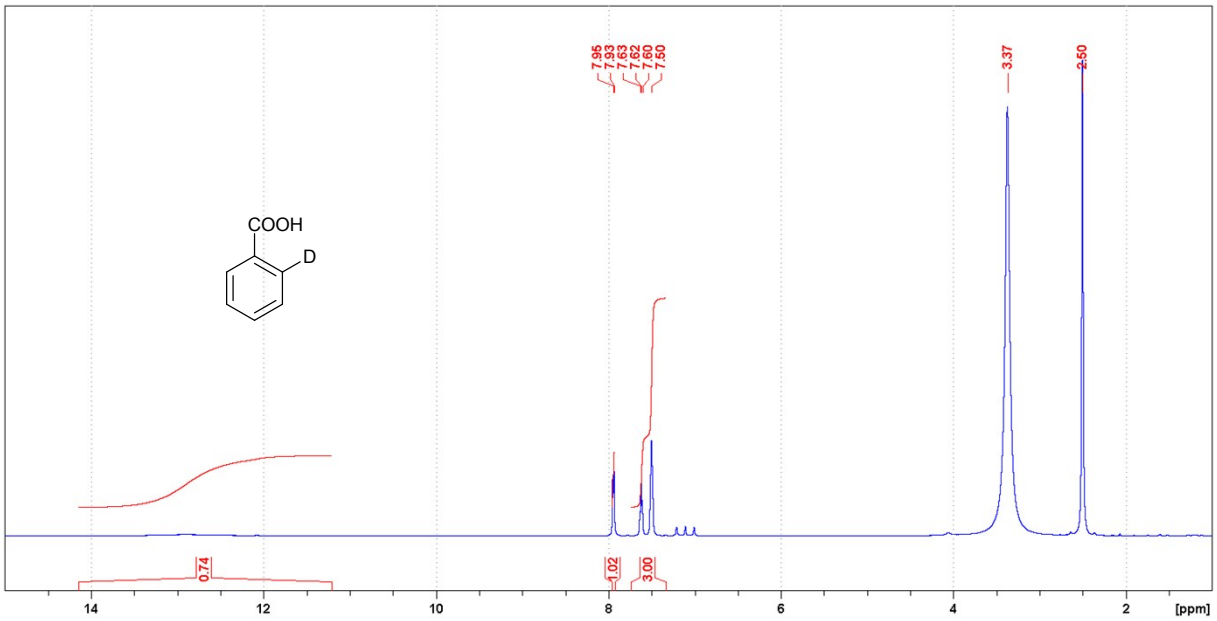


Figure S10. ^{1}H NMR spectrum of **8** measured in DMSO-d_6 at 303 K.

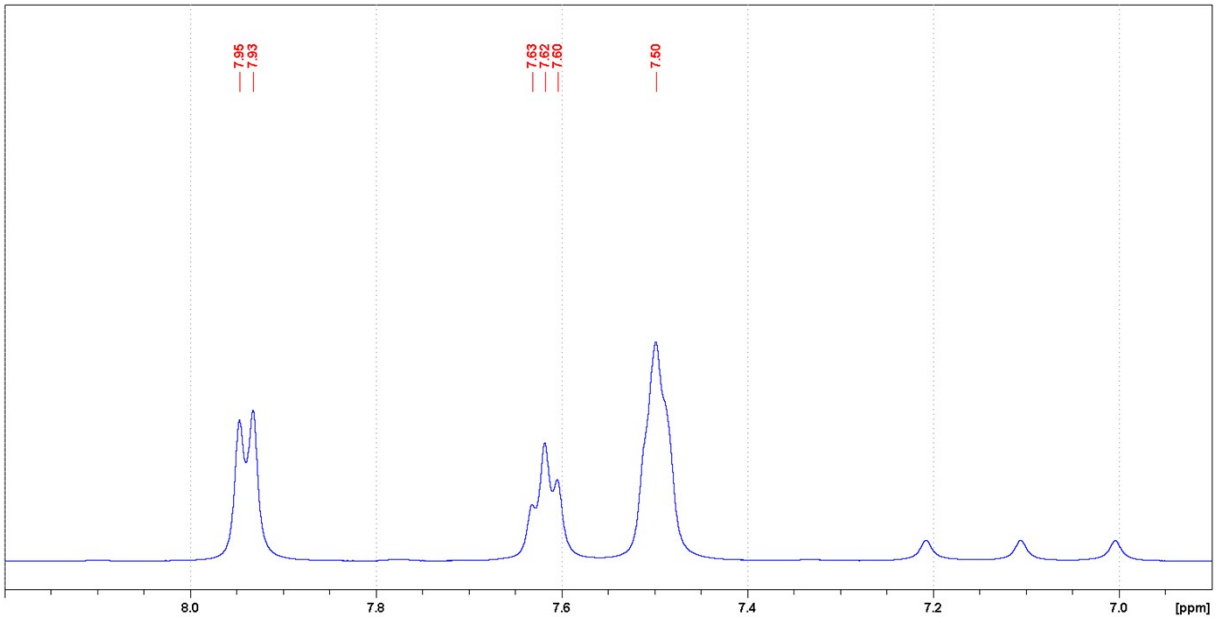


Figure S11. ^{1}H NMR spectrum of **8** measured in DMSO-d_6 at 303 K (aromatic section).

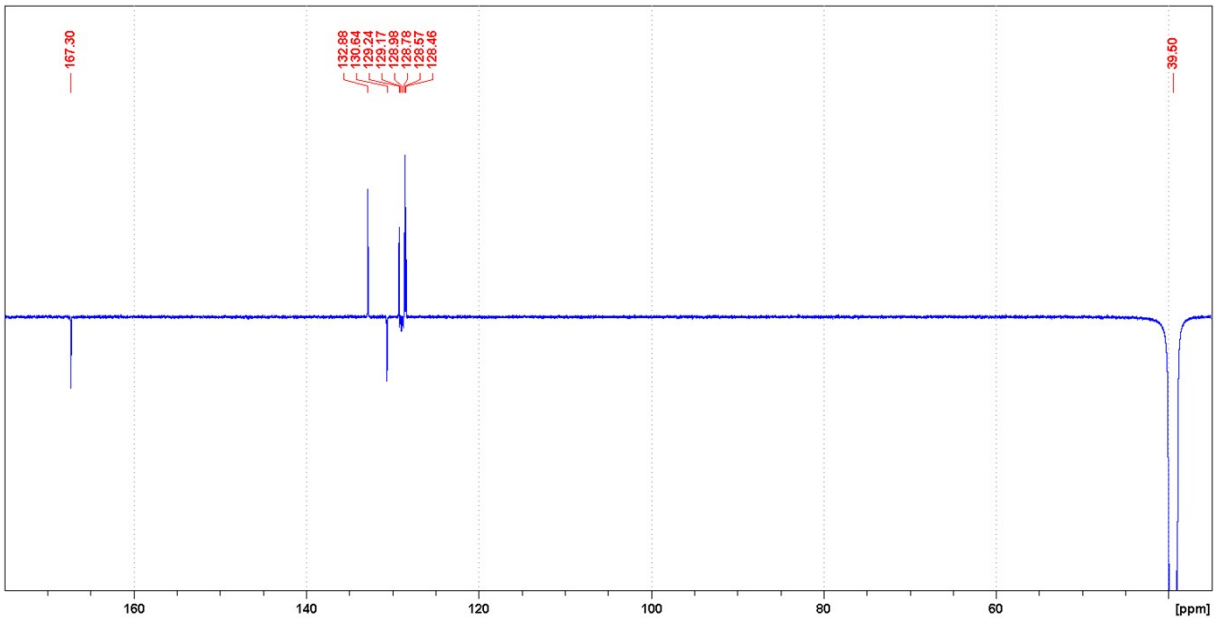


Figure S12. APT NMR spectrum of **8** measured in DMSO-d_6 at 298 K.

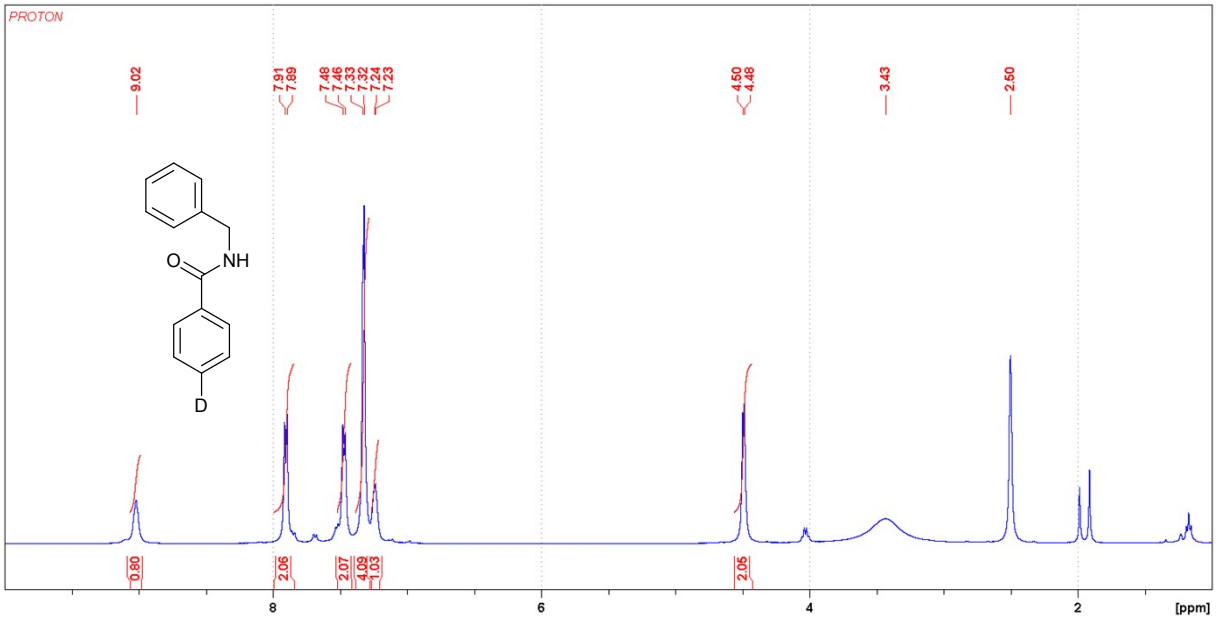


Figure S13. ^{1}H NMR spectrum of **10** measured in DMSO-d_6 at 303 K.

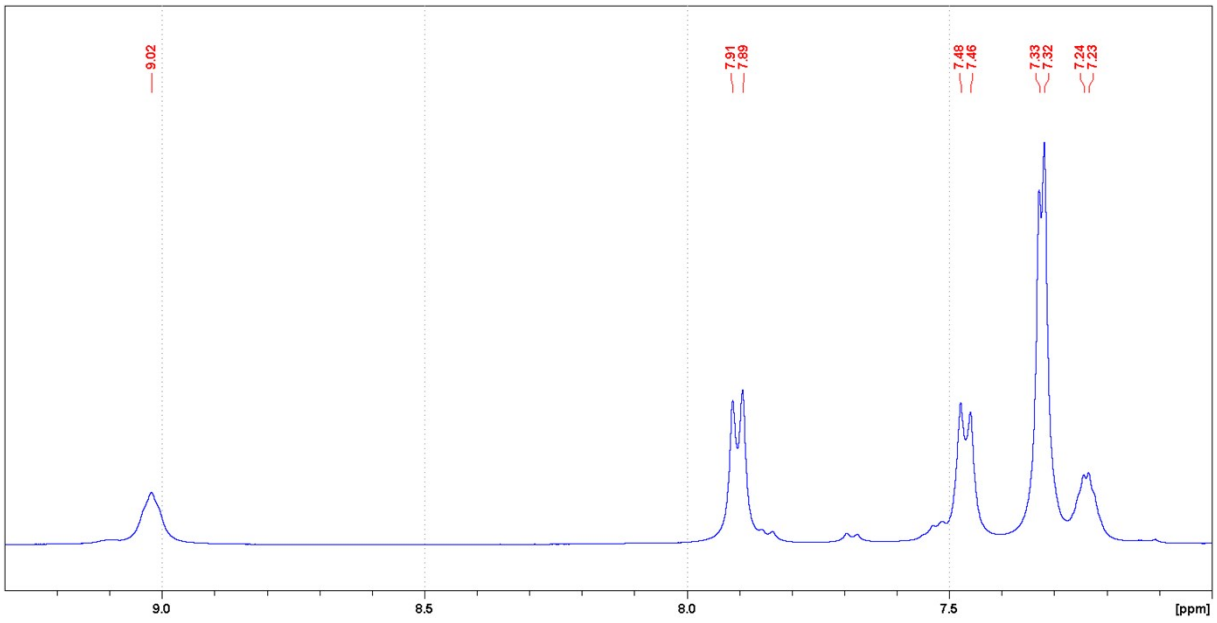


Figure S14. ^{1}H NMR spectrum of **10** measured in DMSO-d_6 at 303 K (aromatic section).

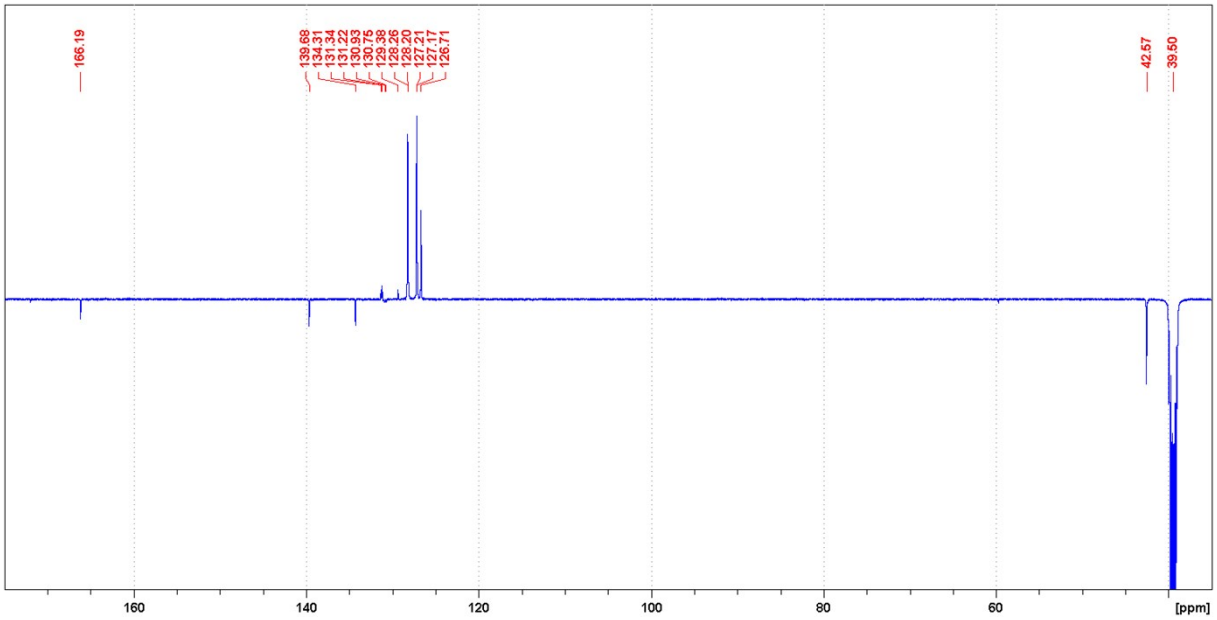


Figure S15. APT NMR spectrum of **10** measured in DMSO-d_6 at 303 K.

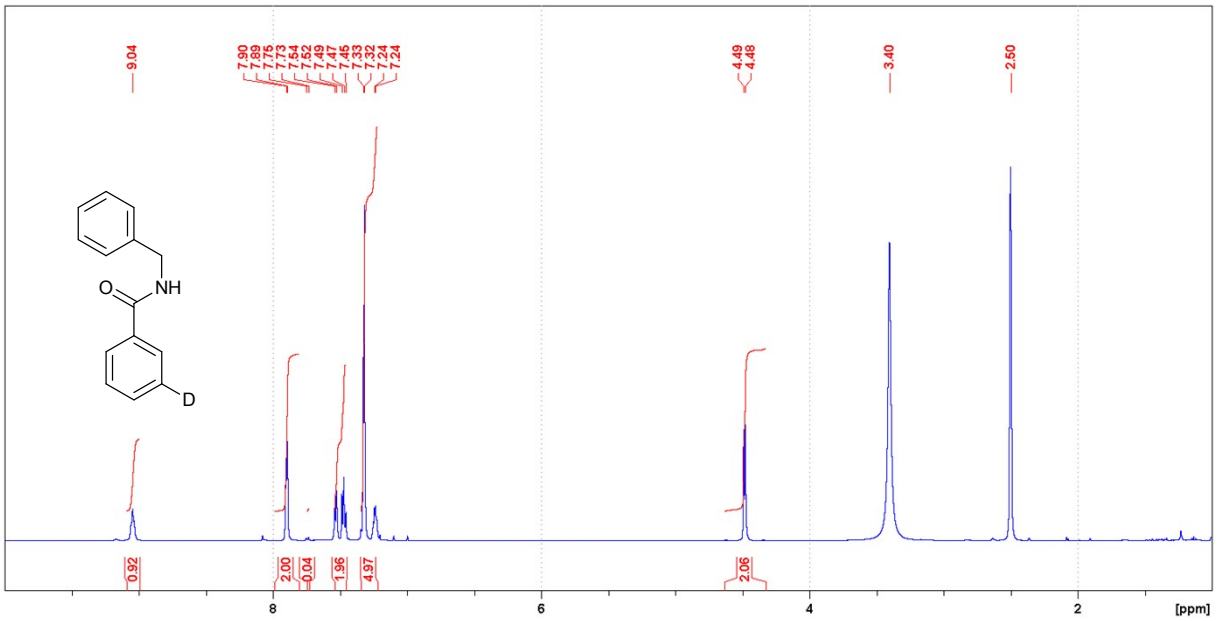


Figure S16. ^{1}H NMR spectrum of **12** measured in DMSO-d_6 at 303 K.

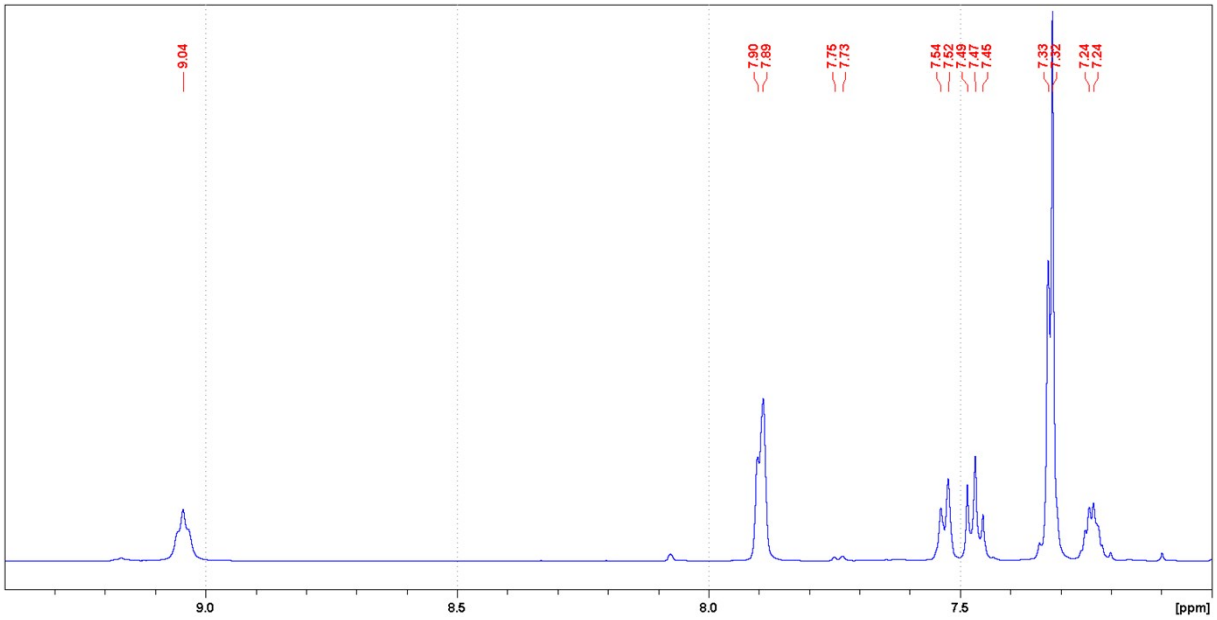


Figure S17. ^{1}H NMR spectrum of **12** measured in DMSO-d_6 at 303 K (aromatic section).

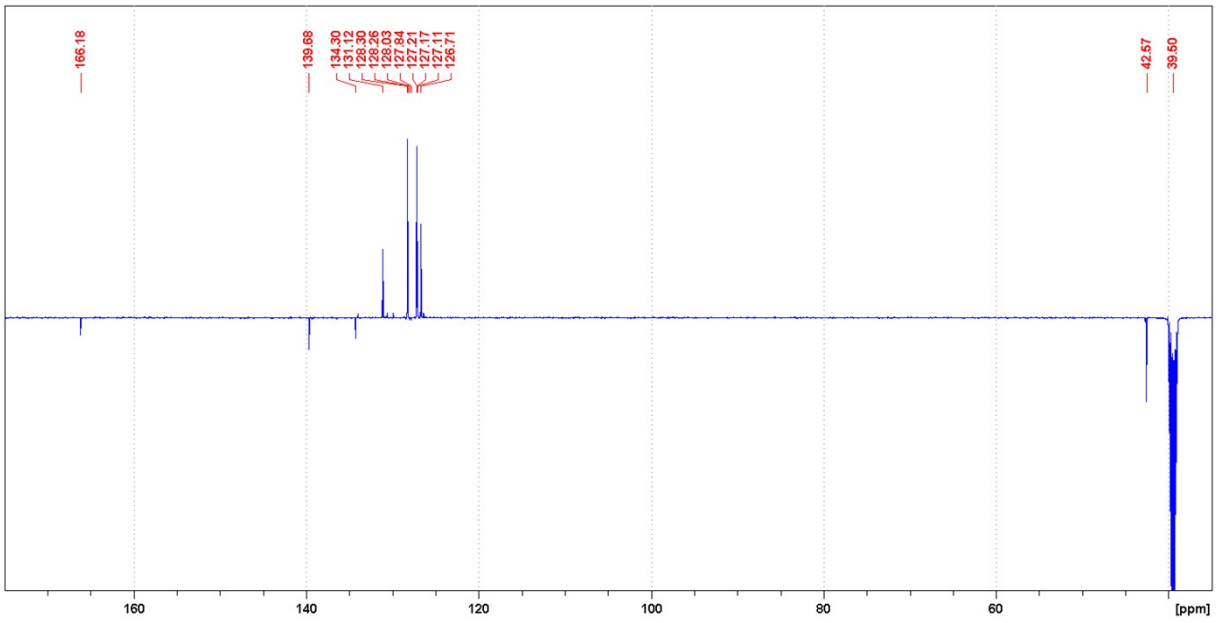


Figure S18. APT NMR spectrum of 1**2** measured in DMSO-d_6 at 303 K.

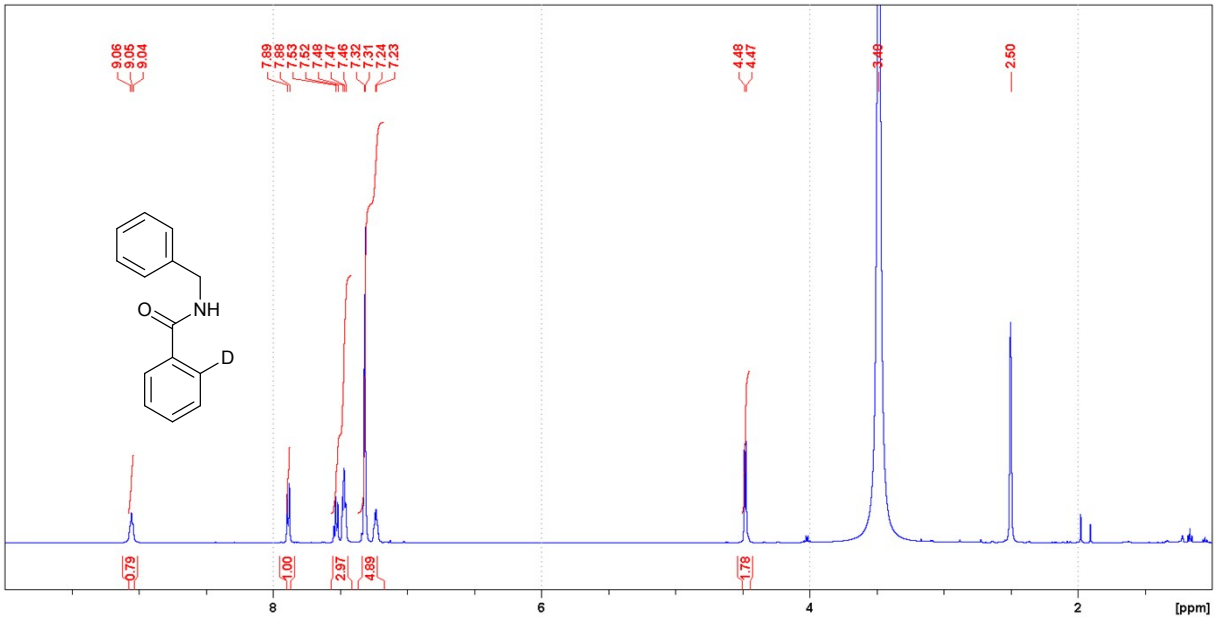


Figure S19. ^{1}H NMR spectrum of **14** measured in DMSO-d_6 at 303 K.

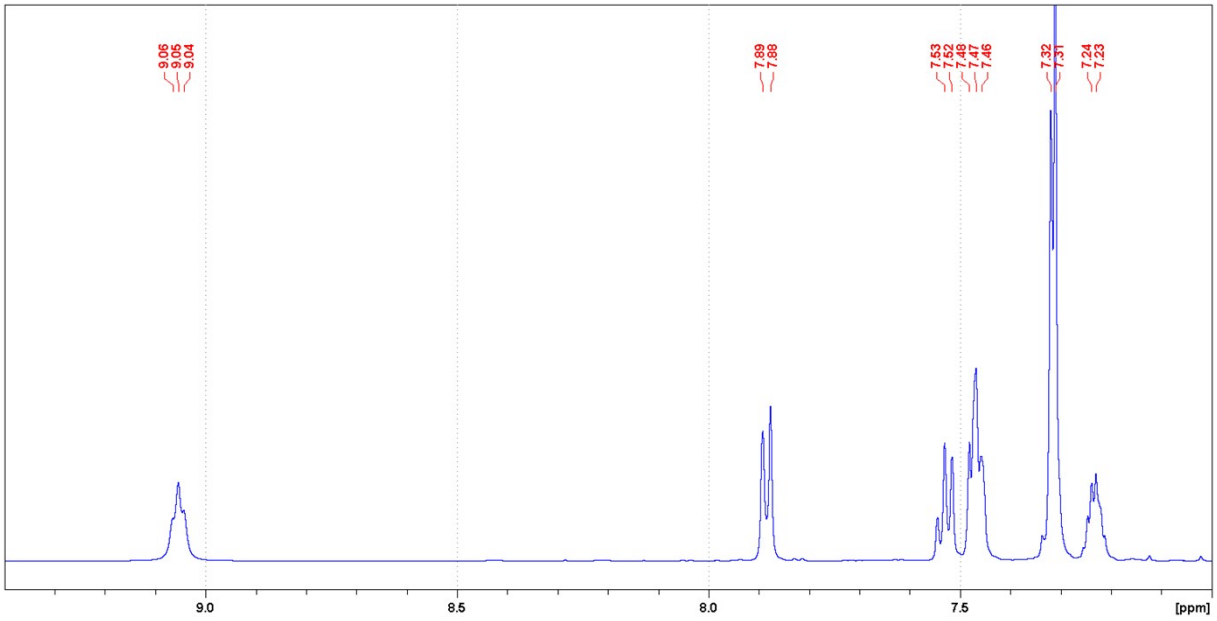


Figure S20. ^{1}H NMR spectrum of **14** measured in DMSO-d_6 at 303 K (aromatic section).

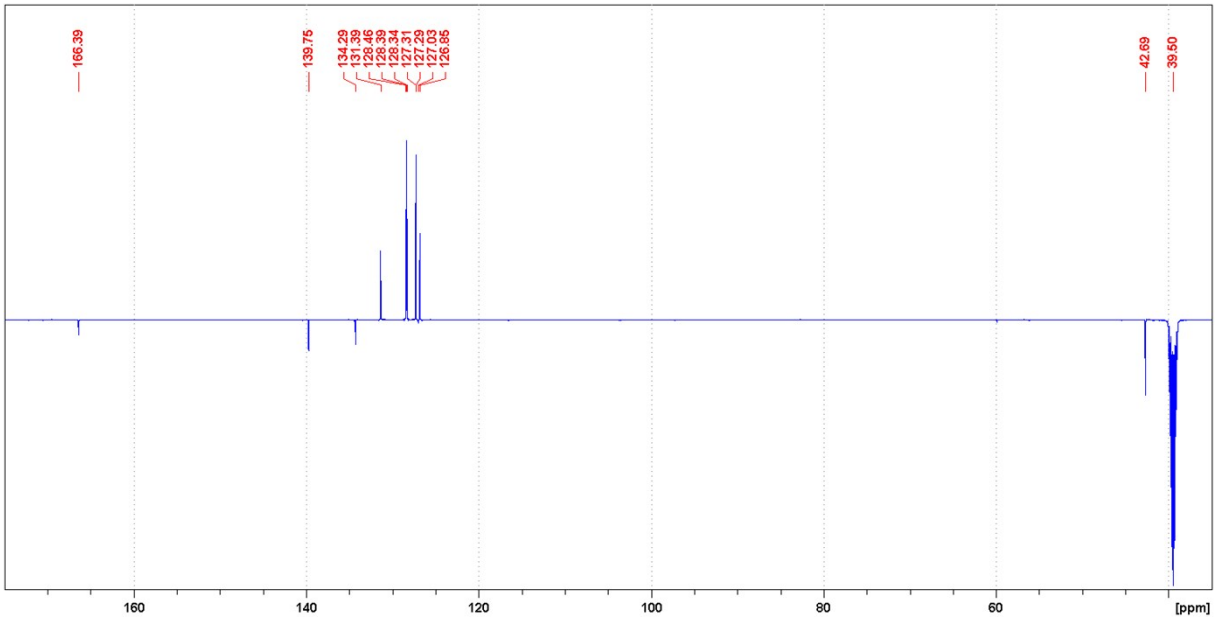


Figure S21. APT spectrum of **14** measured in DMSO-d_6 at 303 K.

[1] M. Oba, *J. Lab. Comp. Radiopharm.* **2015**, *58*, 215-219.
[2] A. I. Meyers, D. L. Temple, D. Haidukewych, E. D. Mihelich, *J. Org. Chem.* **1974**, *39*, 2787-2793.
[3] J. R. L. Smith, M. W. Nee, J. B. Noar, T. C. Bruice, *J. Chem. Soc. Perkin Transact. 2* **1984**, 255-260.