Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Imformation

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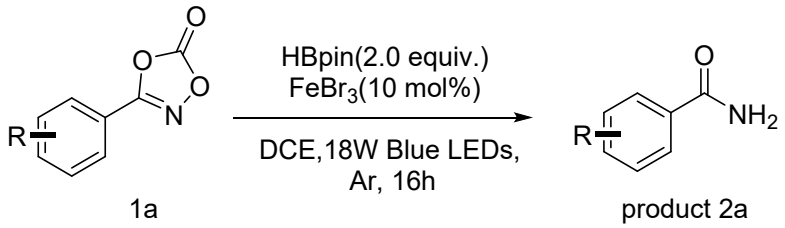
1. General information

^{1}H NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer at room temperature. Chemical shifts (ppm) were referenced to tetramethylsilane (TMS, $\delta = 0$ ppm) in $CDCl_3$ as an internal standard. Data for ^{1}H NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). ^{13}C NMR spectra and ^{19}F NMR spectra were obtained by the same NMR spectrometer and were calibrated with $CDCl_3$ ($\delta = 77.00$ ppm). Data for ^{13}C NMR were reported in terms of chemical shift and multiplicity where appropriate. Melting points were measured on SGW X-4 melting point apparatus and uncorrected. Unless otherwise noted, all reactions were carried out in quartz tubes under argon atmosphere. Anhydrous solvents were from Innochem and dried by standard procedures. HBpin was purchased from J&K Scientific Ltd. DCE was extracted from P_2O_5 by standard method. All other commercially available reagents were from Innochem Chemicals and used as received. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. 1,4,2-Dioxazol-5-ones derivatives 1 were prepared according to the literature. Due to the inclusion of product points by by-product points during TLC monitoring, it is impossible to separate and calculate the separation yield by column chromatography. Unless otherwise stated, all yields are NMR yields. The NMR spectra were obtained by recrystallization of the crude products by using n-hexane + ethyl acetate system after a rough flash chromatography.

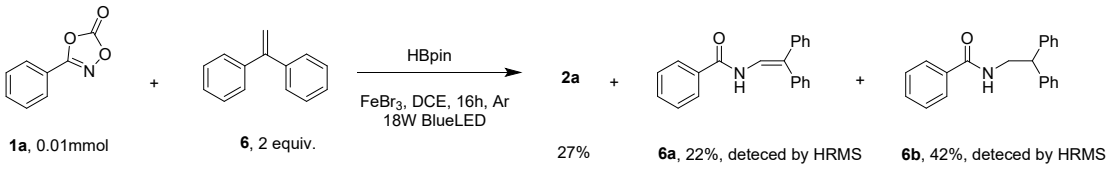
2. General procedure for synthesis of compound 2a



1a product 2a

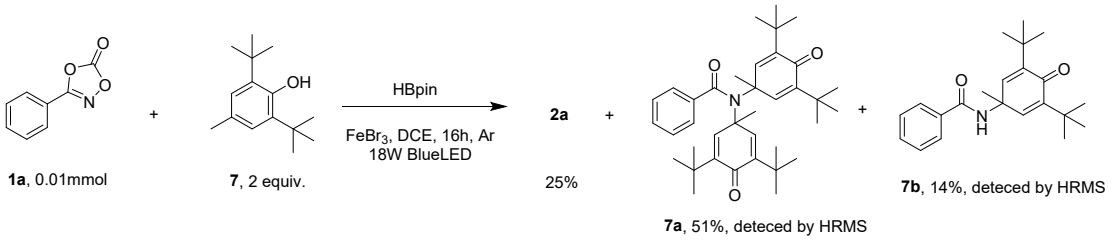
To a 25 mL flame-dried quartz tube was charged with 1a (0.2 mmol, 1.0 equiv.), HBpin(0.4 mmol, 2.0 equiv.), $FeBr_3$(0.02 mmol, 10 mol%) and DCE (3 mL). The mixture was evacuated and backfilled with argon three times. Then the mixture was stirred for 16h under 18 W blue LED irradiation at room temperature. After completion, the mixture was quenched with water (3 mL), and extracted with dichloromethane (10 mL × 3). The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate =5:1 to 1:1) affording the desired products 2a.

3. HRMS results of radical trapping experiment and radical clock experiment



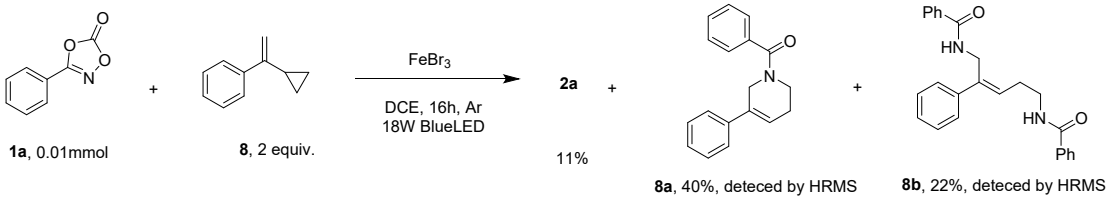
6a HRMS (ESI-TOF) m/z [M +H$^+$] calculated for $C_{21}H_{17}NO$: 300.1382, found: 300.1375.

6b HRMS (ESI-TOF) m/z [M +H$^+$] calculated for $C_{21}H_{19}NO$: 302.1539, found: 302.1530.



7a HRMS (ESI-TOF) m/z [M +H$^+$] calculated for $C_{37}H_{51}NO_3$: 558.3942, found: 558.3931.

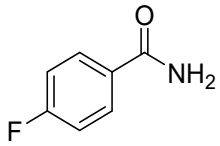
7b HRMS (ESI-TOF) m/z [M +H$^+$] calculated for $C_{22}H_{29}NO_2$: 340.2271, found: 340.2263.



8a HRMS (ESI-TOF) m/z [M +H$^+$] calculated for $C_{18}H_{17}NO$: 264.1383, found: 264.1377.

8b HRMS (ESI-TOF) m/z [M -H$^+$] calculated for $C_{25}H_{22}N_2O_2$: 383.1754, found: 383.1742.

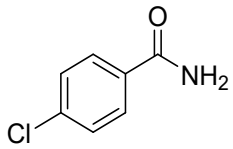
4. Spectroscopic data



4-fluorobenzamide (2aa)

Colorless soild; R_f=0.75 (petroleum ether : EtOAc = 1:1); 85% yield; mp:150-153℃.

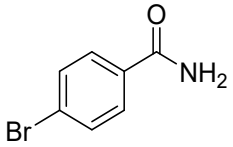
^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.85-7.81 (m, 2H), 7.15-7.10 (m, 2H), 5.96 (s, 2H). **^{13}C NMR (CDCl$_3$, 126 MHz)** δ 168.21, 165.07 (d, $^1J_{CF}$ = 250.0 Hz), 129.76 (d, $^3J_{CF}$ = 7.5 Hz), 129.54 (d, $^4J_{CF}$ = 2.5 Hz), 115.69 (d, $^2J_{CF}$ = 21.2 Hz). **^{19}F NMR (DMSO-*d6*, 376 MHz)** δ -109.63.



4-chlorobenzamide (2ab)

Colorless soild; R_f=0.60 (petroleum ether : EtOAc = 1:1); 93% yield; mp:168-171℃.

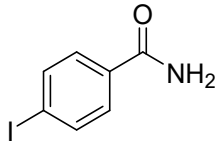
^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 5.96 (s, 2H). **^{13}C NMR (CDCl$_3$, 126 MHz)** δ 168.22, 138.37, 131.72, 128.92, 128.79.



4-bromobenzamide (2ac)

Colorless soild; R_f=0.70 (petroleum ether : EtOAc = 1:1); 73% yield; mp:182-185℃.

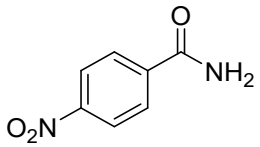
^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.75 (dd, *J* = 6.5, 2.0 Hz, 0.45H), 7.70-7.67 (m, 1.55H), 7.61-7.59 (m, 1.55H), 7.43 (dd, *J* = 6.6, 2.0 Hz, 0.45H), 5.99-5.70 (m, 2H). **^{13}C NMR (CDCl$_3$, 126 MHz)** δ 168.15, 132.16, 131.92, 128.96, 128.93, 128.80, 126.84.



4-iodobenzamide (2ad)

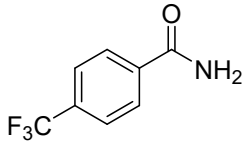
Colorless soild; R_f=0.80 (petroleum ether : EtOAc = 1:1); 84% yield; mp:225-228℃.

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 5.97-5.57 (m, 2H). **^{13}C NMR (CDCl$_3$, 126 MHz)** δ 168.31, 137.91, 132.72, 128.92, 99.14.



4-nitrobenzamide (2ae)

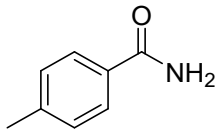
Yellow soild; R_f=0.10 (petroleum ether : EtOAc = 1:1); 89% yield; mp:210-215℃. **^{1}H NMR ($CDCl_3$, 500 MHz)** δ 8.32 (d, *J* = 8.7 Hz, 2H), 7.98 (d, *J* = 8.7 Hz, 2H), 6.09-5.68 (m, 2H). **^{13}C NMR (DMSO-*d*6, 126 MHz)** δ 166.16, 149.02, 139.96, 128.87, 123.38.



4-(trifluoromethyl)benzamide (2af)

Colorless soild; R_f=0.50 (petroleum ether : EtOAc = 1:1); 86% yield; mp:190-193℃.

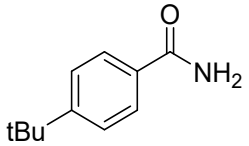
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.93 (d, *J* = 7.9 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 2H), 6.09-5.72 (m, 2H). **^{13}C NMR ($CDCl_3$, 126 MHz)** δ 167.90, 136.59, 133.79 (q, $^2J_{CF3}$ = 32.6 Hz), 127.81, 125.73 (q, $^3J_{CF3}$ = 3.7 Hz), 123.59 (q, $^1J_{CF3}$ = 271.1 Hz). **^{19}F NMR (DMSO-*d6*, 376 MHz)** δ -61.3, -73.5.



4-methylbenzamide (2ag)

Colorless soild; R_f=0.25 (petroleum ether : EtOAc = 1:1); 84% yield; mp:160-163℃.

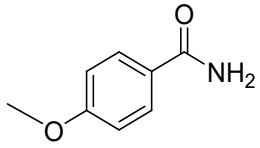
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 5.98 (s, 2H), 2.40 (s, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz)** δ 169.41, 142.53, 130.51, 129.27, 127.38, 21.46.



4-(*tert*-butyl)benzamide (2ah)

Colorless soild; R_f=0.20 (petroleum ether : EtOAc = 1:1); 80% yield; mp:174-178℃.

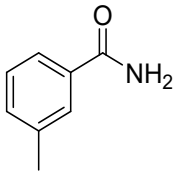
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.06-5.82 (m, 2H), 1.34 (s, 9H). **^{13}C NMR ($CDCl_3$, 126 MHz)** δ 169.29, 155.60, 130.47, 127.23, 125.56, 34.98, 31.14.



4-methoxybenzamide (2ai)

Colorless soild; R_f=0.35 (petroleum ether : EtOAc = 1:1); 88% yield; mp:166-169℃.

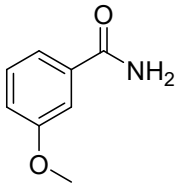
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.78 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 5.87-5.59 (m, 2H), 3.86 (s, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz)** δ 168.80, 162.65, 129.28, 125.56, 113.83, 55.43.



3-methylbenzamide (2aj)

Colorless soild; R_f=0.45 (petroleum ether : EtOAc = 1:1); 72% yield; mp:100-102℃.

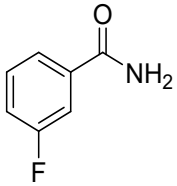
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.65 (s, 1H), 7.58 (s, 1H), 7.34-7.33 (m, 2H), 6.06-5.76 (m, 2H), 2.41 (s, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz)** δ 169.51, 138.53, 133.31, 132.75, 128.49, 128.13, 124.28, 21.32.



3-methoxybenzamide (2ak)

Colorless soild; R_f=0.80 (petroleum ether : EtOAc = 1:1); 75% yield; mp:134-135℃.

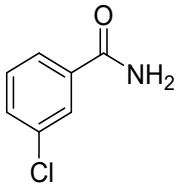
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.41-7.40 (m, 1H), 7.36-7.32 (m, 2H), 7.07 (dt, *J* = 7.2, 2.3 Hz, 1H), 6.10-5.92 (m, 2H), 3.85 (s, 1H). **^{13}C NMR ($CDCl_3$, 126 MHz)** δ 169.22, 159.88, 134.83, 129.60, 119.16, 118.27, 112.61, 55.45.



3-fluorobenzamide (2al)

Colorless soild; R_f=0.75 (petroleum ether : EtOAc = 1:1); 82% yield; mp:130-131℃.

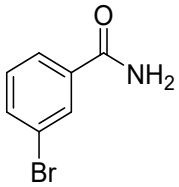
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58-7.53 (m, 2H), 7.43 (q, *J* = 6.8 Hz, 1H), 7.23 (t, *J* = 8.2 Hz, 1H), 6.11 (s, 2H). **^{13}C NMR ($CDCl_3$, 126 MHz)** δ 168.12, 162.77 (d, $^1J_{CF}$ = 246.5 Hz), 135.67 (d, $^5J_{CF}$ = 7.0 Hz), 130.31 (d, $^4J_{CF}$ = 7.6 Hz), 122.80 (d, $^6J_{CF}$ = 2.9 Hz), 119.02 (d, $^3J_{CF}$ = 21.1 Hz), 114.74 (d, $^2J_{CF}$ = 22.8 Hz). **^{19}F NMR (DMSO-*d6*, 376 MHz)** δ -113.0.



3-chlorobenzamide (2am)

Colorless soild; R_f=0.70 (petroleum ether : EtOAc = 1:1); 74% yield; mp:135-137℃.

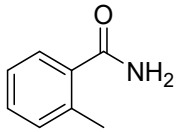
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.81 (s, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 6.04-5.82 (m, 2H). **^{13}C NMR ($CDCl_3$, 126 MHz)** δ 167.87, 135.13, 134.88, 132.05, 129.96, 127.74, 125.39.



3-bromobenzamide (2an)

Colorless soild; R_f=0.80 (petroleum ether : EtOAc = 1:1); 70% yield; mp:155-156℃.

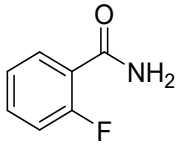
^{1}H NMR (DMSO-*d*6, 500 MHz) δ 8.08 (s, 1H), 8.05 (t, *J* = 1.7 Hz, 1H), 7.88-7.87 (m, 1H), 7.72 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.49 (s, 1H), 7.42 (t, *J* = 7.9 Hz, 1H). **^{13}C NMR (DMSO-*d*6, 126 MHz)** δ 166.26, 136.45, 133.88, 130.43, 130.12, 126.48, 121.56.



2-methylbenzamide (2ao)

Colorless soild; R_f=0.85 (petroleum ether : EtOAc = 1:1); 60% yield; mp:139-141℃.

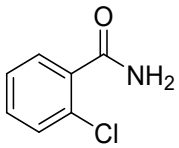
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.47-7.45 (m, 1H), 7.34 (td, *J* = 7.5, 1.5 Hz, 1H), 7.25-7.20 (m, 2H), 5.69-5.63 (m, 2H), 2.51 (s, 3H). **^{13}C NMR (DMSO-*d6*, 126 MHz)** δ 170.94, 137.02, 135.02, 130.36, 129.06, 126.92, 125.85, 19.48.



2-fluorobenzamide (2ap)

Colorless soild; R_f=0.85 (petroleum ether : EtOAc = 1:1); 70% yield; mp:115-116℃.

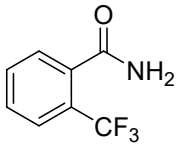
^{1}H NMR (DMSO-*d*6, 500 MHz) δ 7.65 (td, *J* = 7.6, 1.7 Hz, 2H), 7.61 (s, 1H), 7.54-7.49 (m, 1H), 7.28-7.25 (m, 2H). **^{13}C NMR (DMSO-*d*6, 126 MHz)** δ 165.16, 159.24 (d, $^1J_{CF}$ = 247.5 Hz), 132.39 (d, $^4J_{CF}$ = 8.3 Hz), 130.16 (d, $^6J_{CF}$ = 2.8 Hz), 124.33 (d, $^5J_{CF}$ = 3.1 Hz), 123.81 (d, $^3J_{CF}$ = 14.2 Hz), 116.02 (d, $^2J_{CF}$ = 22.3 Hz). **^{19}F NMR (DMSO-*d6*, 376 MHz)** δ -113.78.



2-chlorobenzamide (2aq)

Colorless soild; R_f=0.70 (petroleum ether : EtOAc = 1:1); 68% yield; mp:138-139℃.

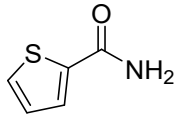
^{1}H NMR (DMSO-*d*6, 500 MHz) δ 7.84 (s, 1H), 7.55 (s, 1H), 7.48-7.46 (m, 1H), 7.44-7.40 (m, 2H), 7.38-7.35 (m, 1H). **^{13}C NMR (DMSO-*d*6, 126 MHz)** δ 168.05, 137.09, 130.45, 129.56, 129.52, 128.59, 126.92.



2-(trifluoromethyl)benzamide (2ar)

Colorless soild; R_f=0.65 (petroleum ether : EtOAc = 1:1); 75% yield; mp:156-158℃.

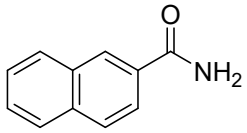
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.71 (d, J = 8.0 Hz,1H), 7.61 (s,1H), 7.60(s, 1H), 7.58-7.54 (m,1H), 6.11 (s, 1H), 5.82 (s, 1H). **^{13}C NMR ($CDCl_3$, 126 MHz)** δ 169.75, 134.98, 132.06, 130.12, 128.61, 127.23 (q, $^2J_{CF3}$ = 32.0 Hz), 126.39 (q, $^3J_{CF3}$ = 4.6 Hz), 123.53 (q, $^1J_{CF3}$ = 272.2 Hz). **^{19}F NMR (DMSO-*d6*, 376 MHz)** δ -57.86.



thiophene-2-carboxamide (2as)

Colorless soild; R_f=0.80 (petroleum ether : EtOAc = 1:1); 85% yield; mp:185-188℃.

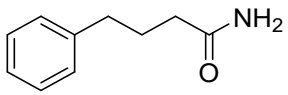
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.54 (s, 2H), 7.10 (d, J = 3.4 Hz, 1H), 5.69 (s, 2H). **^{13}C NMR ($CDCl_3$, 126 MHz)** δ 163.52, 137.77, 130.89, 129.29, 127.77.



2-naphthamide (2at)

Colorless soild; R_f=0.80 (petroleum ether : EtOAc = 1:1); 85% yield; mp:188-189℃.

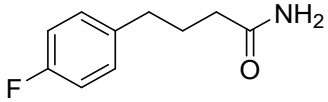
^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.50 (s, 1H), 8.15 (s, 1H), 8.01-7.96 (m, 4H), 7.62-7.56 (m, 2H), 7.44 (s, 1H). **^{13}C NMR ($CDCl_3$, 126 MHz)** δ 167.89, 134.10, 132.10, 131.59, 128.79, 127.75, 127.67, 127.51, 127.48, 126.56, 124.34.



4-phenylbutanamide (4aa)

Colorless soild; R_f=0.70 (petroleum ether : EtOAc = 1:1); 52% yield; mp:104-106℃.

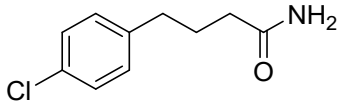
^{1}H NMR (DMSO-*d6*, 500 MHz) δ 7.30-7.27 (m, 2H), 7.21-7.18 (m, 2H), 5.39-5.38 (m, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.22 (t, *J* = 7.4 Hz, 2H), 2.02-1.96 (m, 2H). **^{13}C NMR (DMSO-*d6*, 126 MHz)** δ 175.05, 141.36, 128.47, 128.39, 125.99, 35.07, 34.94, 26.81.



4-(4-fluorophenyl)butanamide (4ab)

Colorless soild; R_f=0.70 (petroleum ether : EtOAc = 1:1); 56% yield; mp:116-119℃.

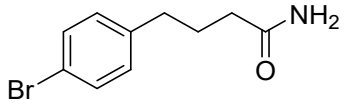
^{1}H NMR (DMSO-*d*6, 500 MHz) δ 7.25-7.19 (m, 3H), 7.11-7.06 (m, 2H), 6.71 (s, 1H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.04 (t, *J* = 7.3 Hz, 2H), 1.79-1.73 (m, 2H). **^{13}C NMR (DMSO-*d*6, 126 MHz)** δ 173.89, 160.55 (d, $^{1}J_{CF}$ = 241.3 Hz), 137.89 (d, $^{4}J_{CF}$ = 3.2 Hz), 129.96 (d, $^{3}J_{CF}$ = 7.8 Hz), 114.85 (d, $^{2}J_{CF}$ = 20.7 Hz), 34.36, 33.73, 26.87. **^{19}F NMR (DMSO-*d6*, 376 MHz)** δ -117.74.



4-(4-chlorophenyl)butanamide (4ac)

Colorless soild; R_f=0.85 (petroleum ether : EtOAc = 1:1); 57% yield; mp:111-113℃.

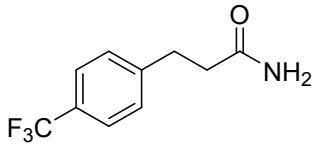
^{1}H NMR (DMSO-*d*6, 500 MHz) δ 7.33-7.31 (m, 2H), 7.24 (s, 1H), 7.22-7.20 (m, 2H), 6.70 (s, 1H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.04 (t, *J* = 7.4 Hz, 2H), 1.79-1.73 (m, 2H). **^{13}C NMR (DMSO-*d*6, 126 MHz)** δ 173.86, 140.79, 130.28, 130.13, 128.11, 34.30, 33.85, 26.59.



4-(4-bromophenyl)butanamide (4ad)

Colorless soild; R_f=0.70 (petroleum ether : EtOAc = 1:1); 60% yield; mp:153-156℃.

^{1}H NMR (DMSO-*d*6, 500 MHz) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.26 (s, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.73 (s, 1H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.04 (t, *J* = 7.4 Hz, 2H), 1.79-1.73 (m, 2H). **^{13}C NMR (DMSO-*d*6, 126 MHz)** δ 173.93, 141.23, 131.07, 130.59, 118.73, 34.33, 33.93, 26.57.

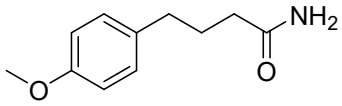


3-(4-(trifluoromethyl)phenyl)propenamide (4ae)

Colorless soild; R_f=0.70 (petroleum ether : EtOAc = 1:1); 55% yield; mp:188-189℃.

^{1}H NMR (DMSO-*d*6, 500 MHz) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.33 (s, 1H), 6.81 (s, 1H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.40 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR (DMSO-*d*6, 126 MHz)** δ 173.10, 146.46, 129.04, 126.69 (q, $^{2}J_{CF3}$ = 31.6 Hz), 125.01

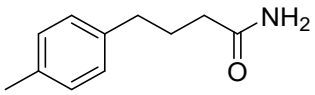
(q, $^{3}J_{CF3}$ = 3.7 Hz), 124.43 (q, $^{1}J_{CF3}$ = 272.0 Hz), 36.05, 30.56. **^{19}F NMR (DMSO-*d6*, 376 MHz)** δ -60.83.



4-(4-methoxyphenyl)butanamide (4af)

Colorless soild; R_f=0.70 (petroleum ether : EtOAc = 1:1); 65% yield; mp:125-126℃.

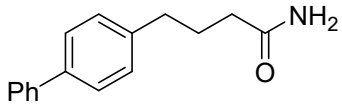
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.10 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.31 (s, 2H), 2.62 (t, *J* = 7.4 Hz, 2H), 2.21 (t, *J* = 7.4 Hz, 2H), 1.98-1.92 (m, 2H). **^{13}C NMR ($CDCl_3$, 126 MHz)** δ 174.97, 157.95, 129.38, 114.31, 113.86, 55.26, 34.89, 34.17, 27.06.



4-(p-tolyl)butanamide (4ag)

Colorless soild; R_f=0.60 (petroleum ether : EtOAc = 1:1); 59% yield; mp:133-134℃.

^{1}H NMR (DMSO-*d*6, 500 MHz) δ 7.24 (s, 1H), 7.09-7.05 (m, 4H), 6.70 (s, 1H), 2.51 (t, *J* = 7.3 Hz, 2H), 2.26 (s, 3H), 2.04 (t, *J* = 7.4 Hz, 2H), 1.78-1.72 (m, 2H). **^{13}C NMR (DMSO-*d*6, 126 MHz)** δ 173.99, 138.65, 134.51, 128.79, 128.13, 34.48, 34.23, 26.90, 20.56.



4-([1,1'-biphenyl]-4-yl)butanamide (4ah)

Colorless soild; R_f=0.45 (petroleum ether : EtOAc = 1:1); 54% yield; mp:204-208℃.

^{1}H NMR (DMSO-*d*6, 500 MHz) δ 7.66-7.63 (m, 2.5H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 2.5H), 6.74 (s, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.10 (t, *J* = 7.4 Hz, 2H), 1.85-1.79 (m, 2H). **^{13}C NMR (DMSO-*d*6, 126 MHz)** δ 173.96, 141.09, 140.07, 137.65, 128.88, 128.84, 127.10, 126.53, 126.42, 34.50, 34.24, 26.72.

5. Reference

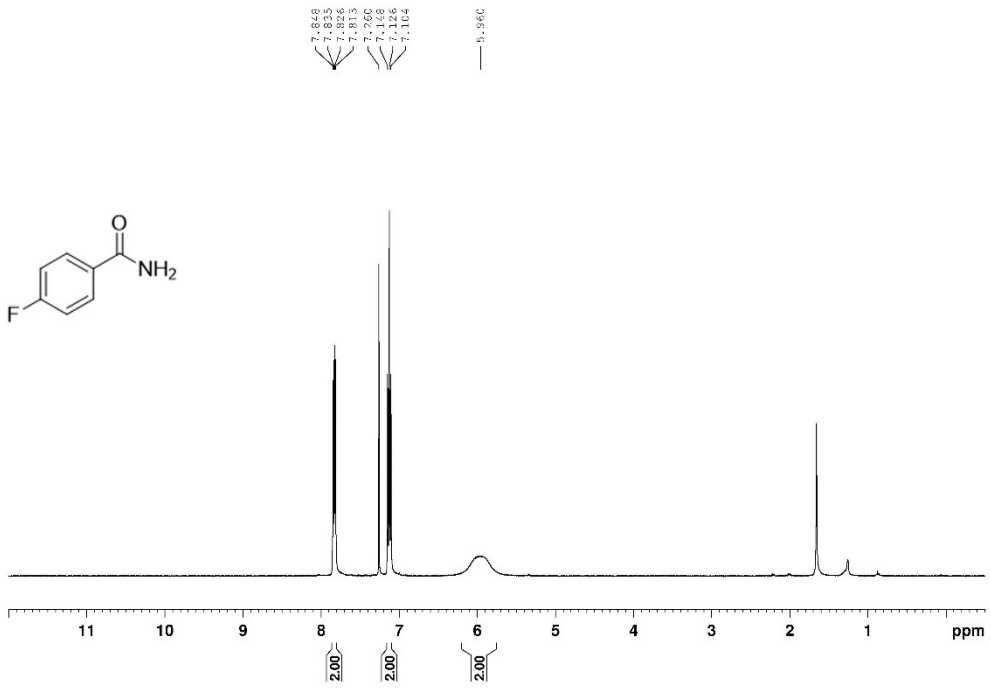
1. Guo, Y.; Wang, R. Y.; Kang, J. X.; Ma, Y. N.; Xu, C. Q.; Li, J.; Chen, X., Efficient synthesis of primary and secondary amides via reacting esters with alkali metal amidoboranes. *Nat Commun* **2021,** *12* (1), 5964.

2. Liu, C. F.; Luo, X.; Wang, H.; Koh, M. J., Catalytic Regioselective Olefin Hydroarylation(alkenylation) by Sequential Carbonickelation-Hydride Transfer. *J Am Chem Soc* **2021,** *143* (25), 9498-9506.

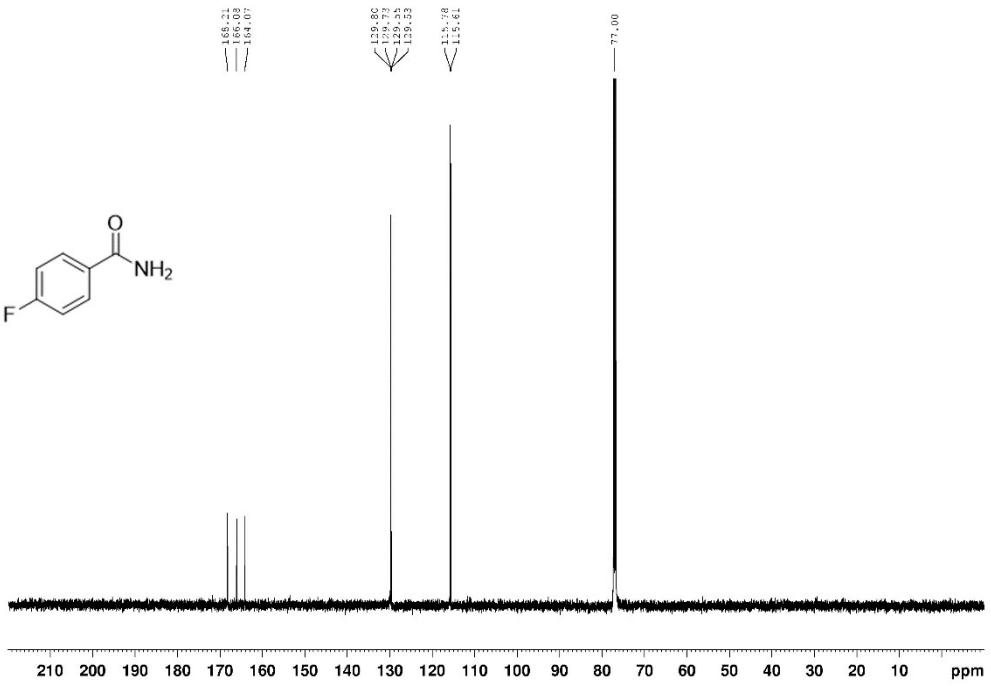
3. Wan, Y.; Ramírez, E.; Ford, A.; Bustamante, V.; Li, G., Fe-Catalyzed C(sp3)–H Diversification toward γ-Functionalized Amides via Iron Nitrenoid: Mechanistic Insights and Applications. *ACS Catalysis* **2023,** *13* (21), 14023-14030.

6. NMR spectra

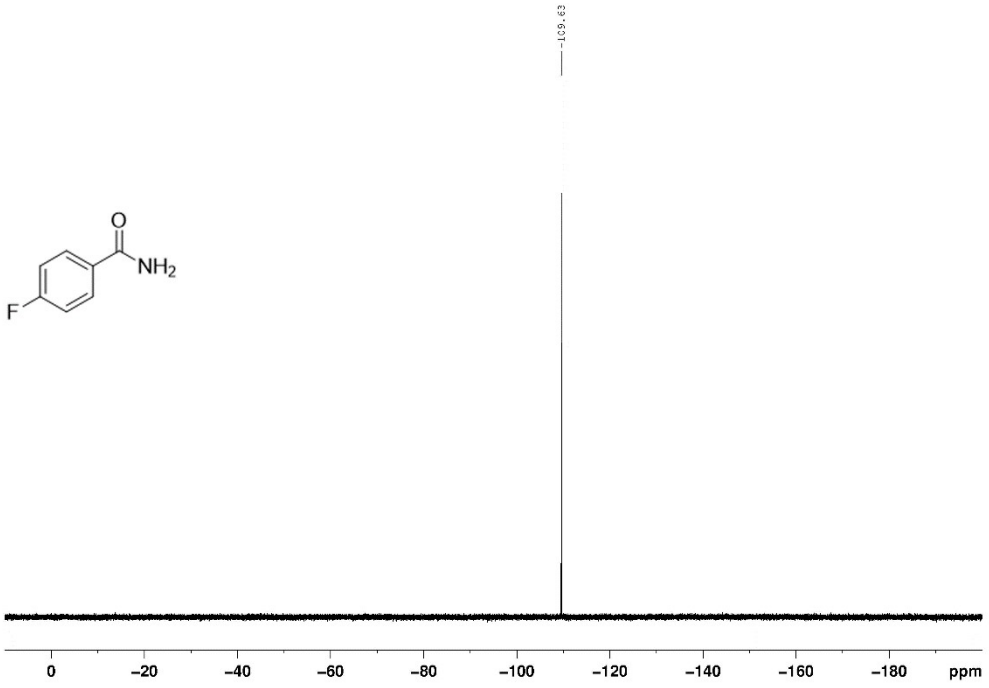
2aa, ^{1}H NMR, 500 M, $CDCl_3$



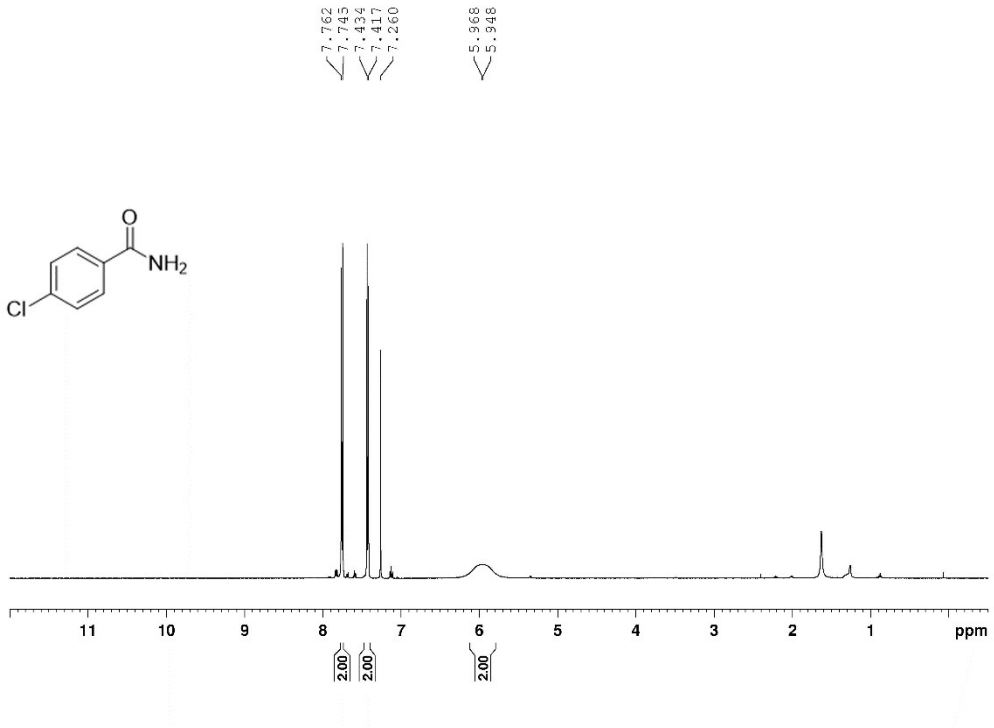
2aa, ^{13}C NMR, 126 M, $CDCl_3$



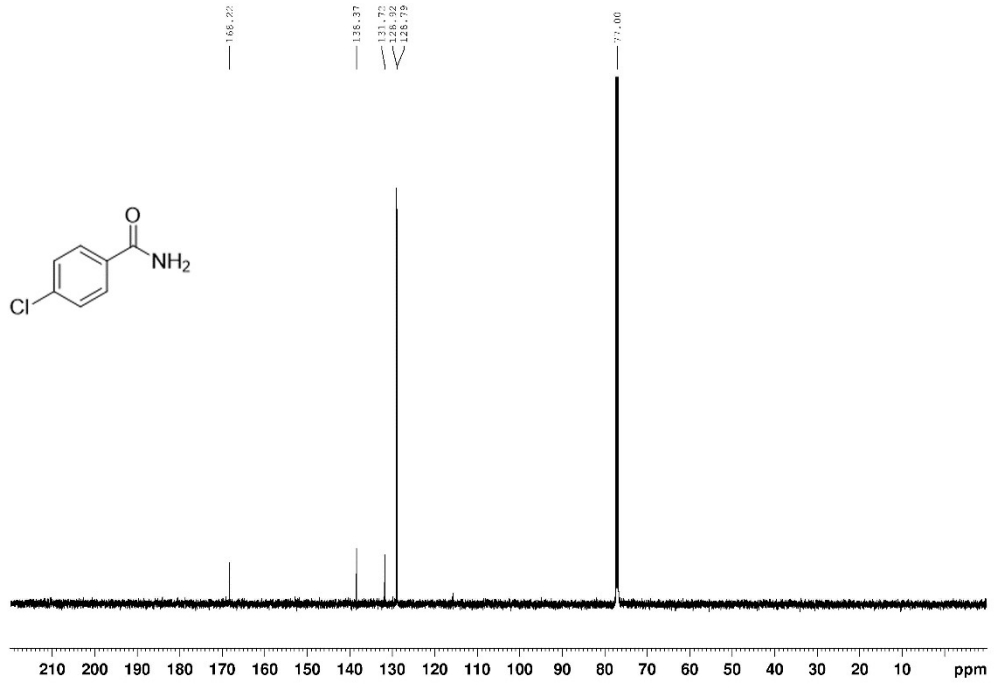
2aa, ^{19}F NMR, 376 M, DMSO-*d6*



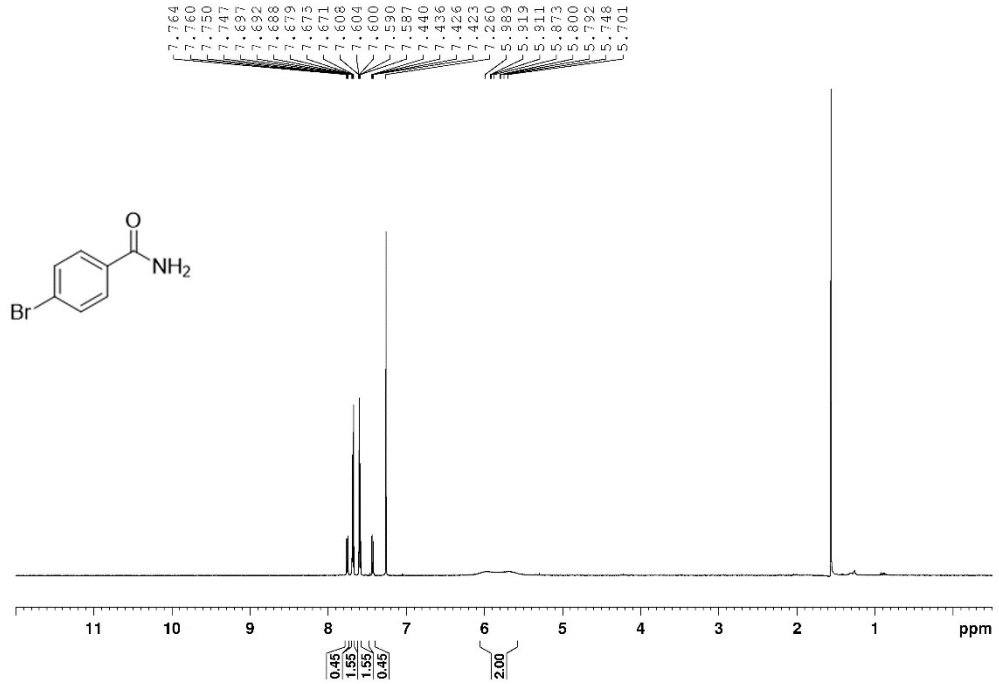
2ab, ^{1}H NMR, 500 M, $CDCl_3$



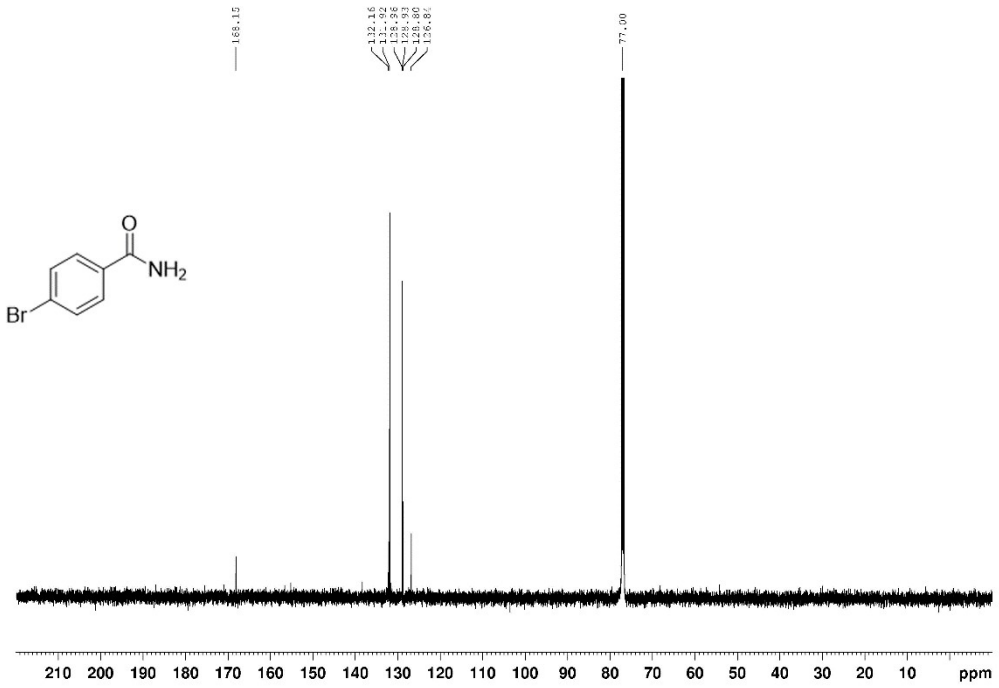
2ab, ^{13}C NMR, 126 M, $CDCl_3$



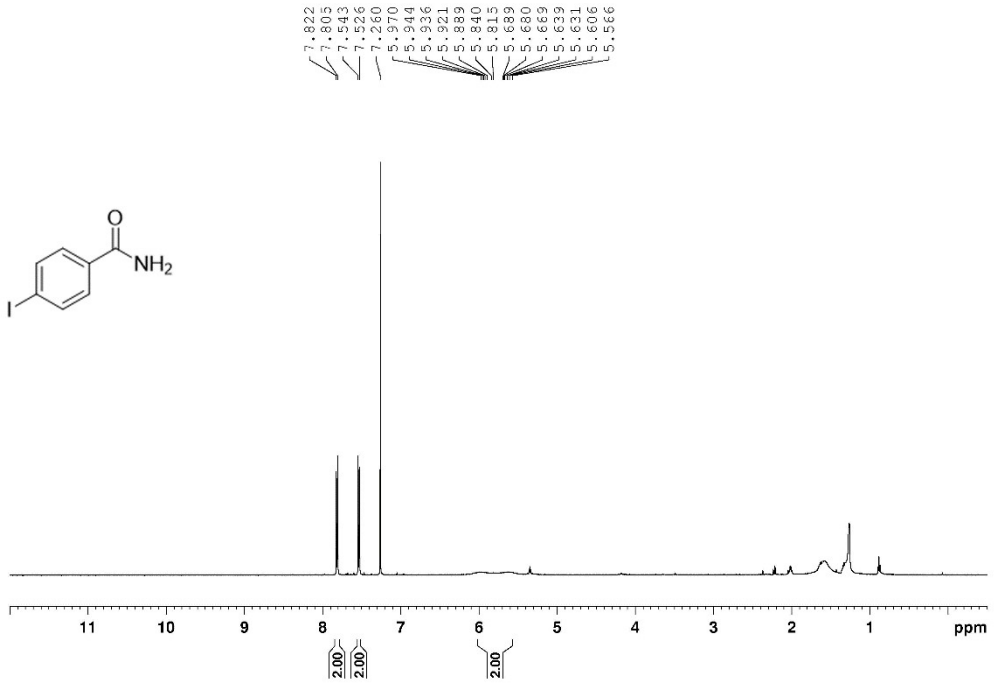
2ac, ^{1}H NMR, 500 M, $CDCl_3$



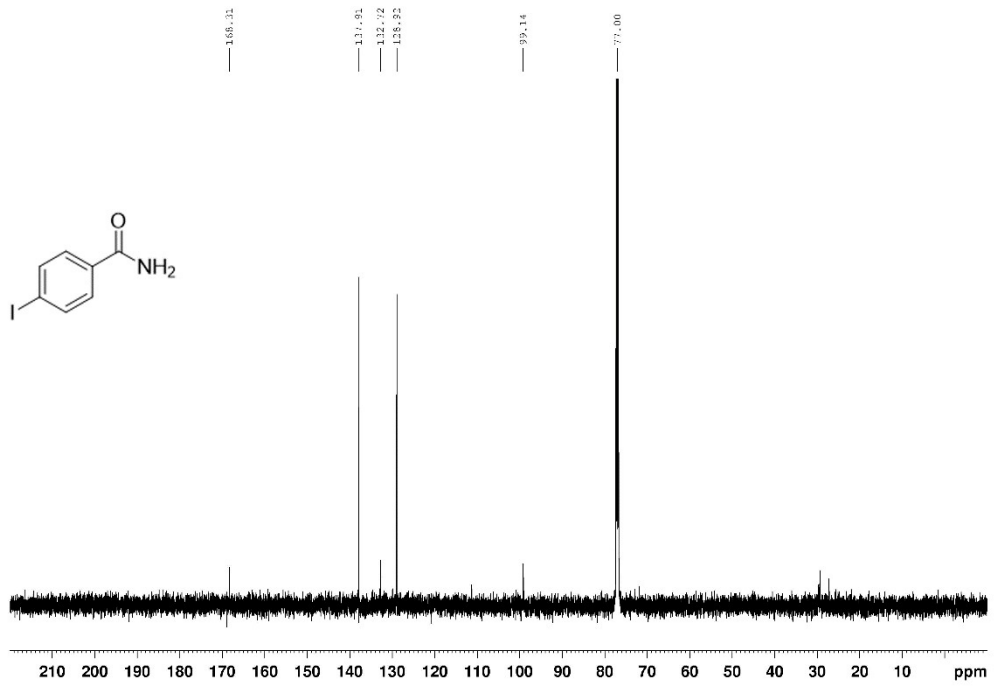
2ac, ^{13}C NMR, 126 M, $CDCl_3$



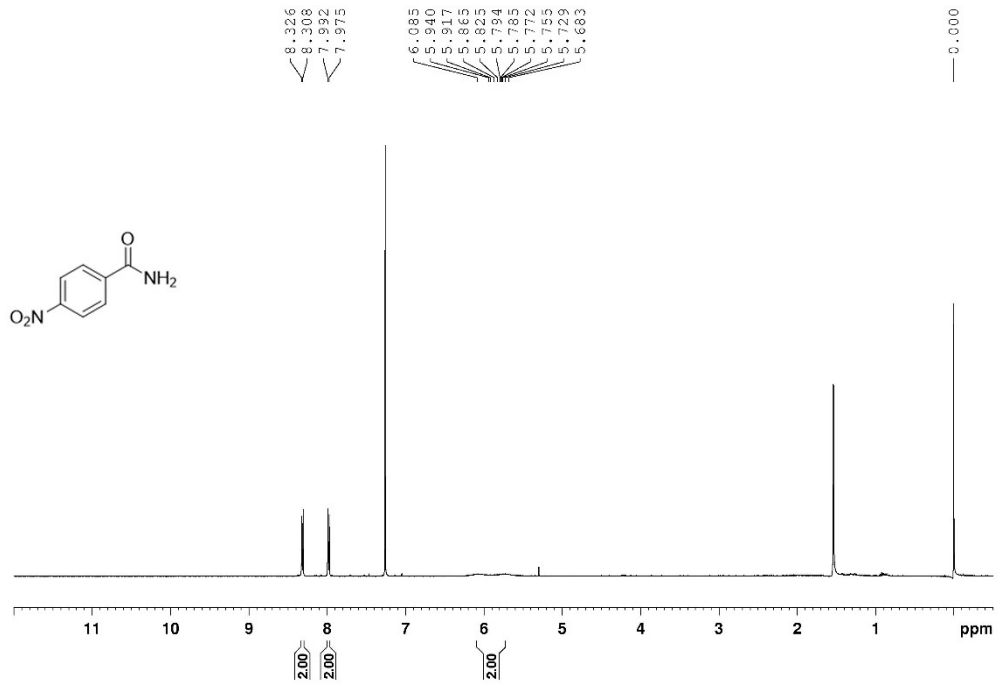
2ad, ^{1}H NMR, 500 M, $CDCl_3$



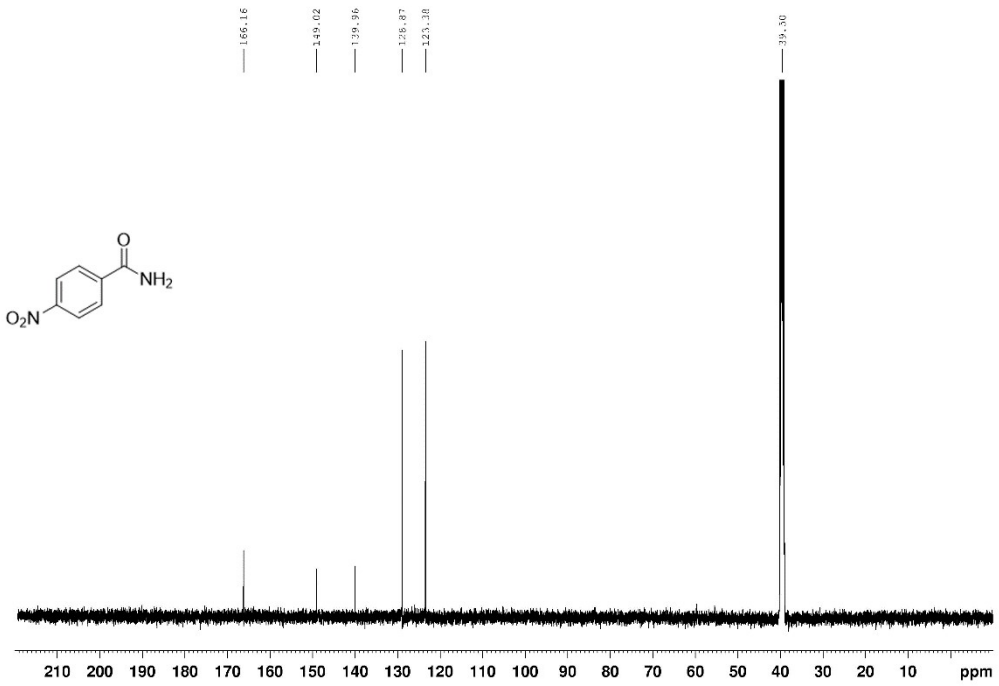
2ad, ^{13}C NMR, 126 M, $CDCl_3$



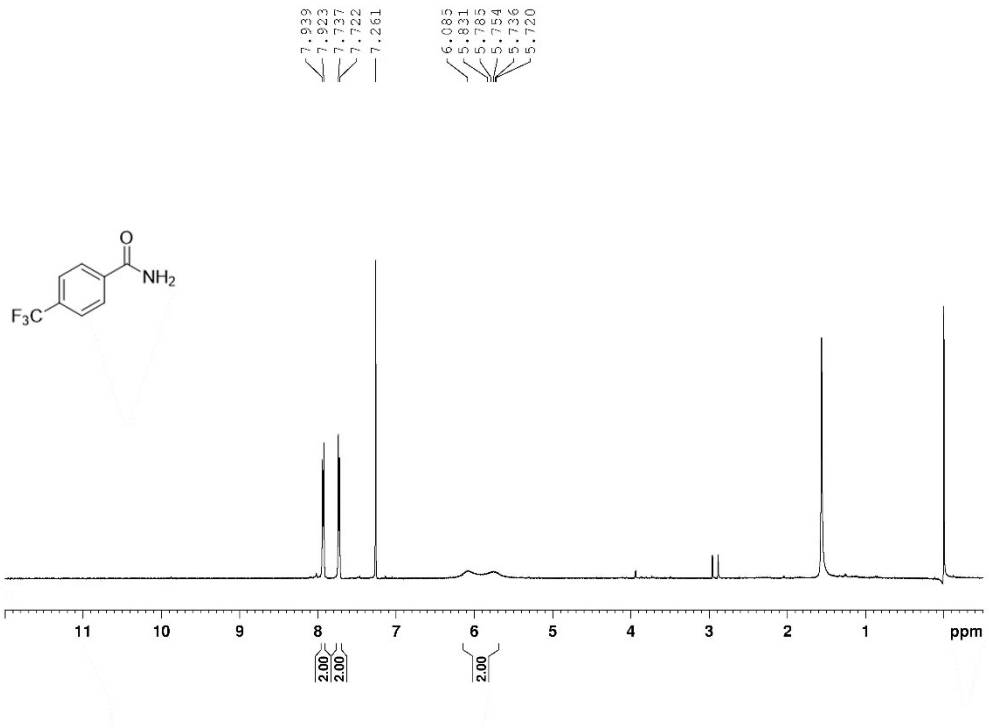
2ae, ^{1}H NMR, 500 M, $CDCl_3$



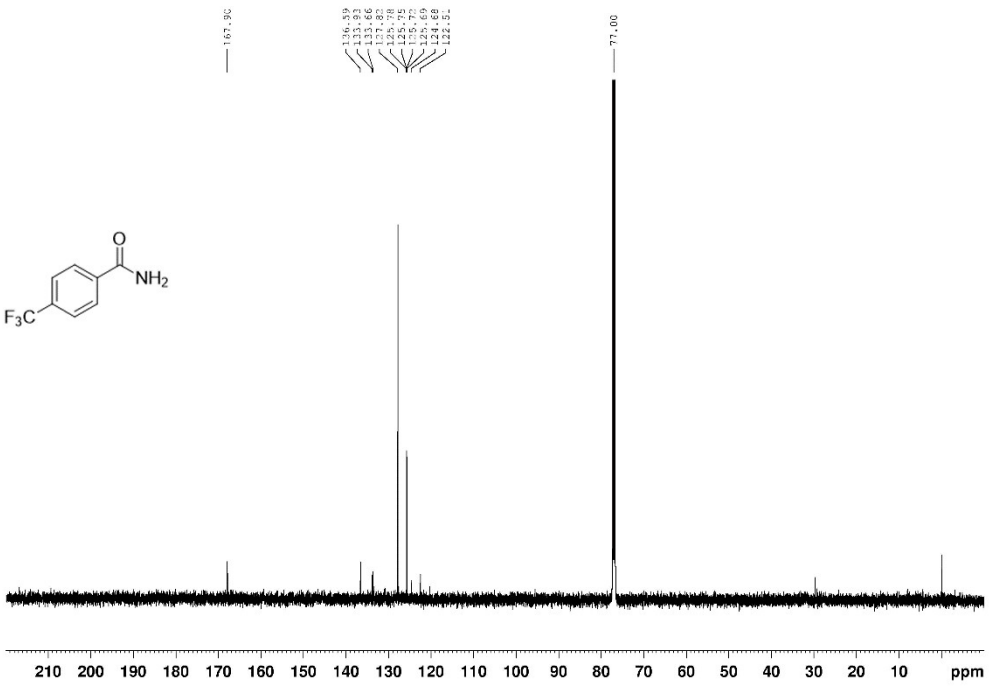
2ae, ^{13}C NMR, 126 M, DMSO-*d6*



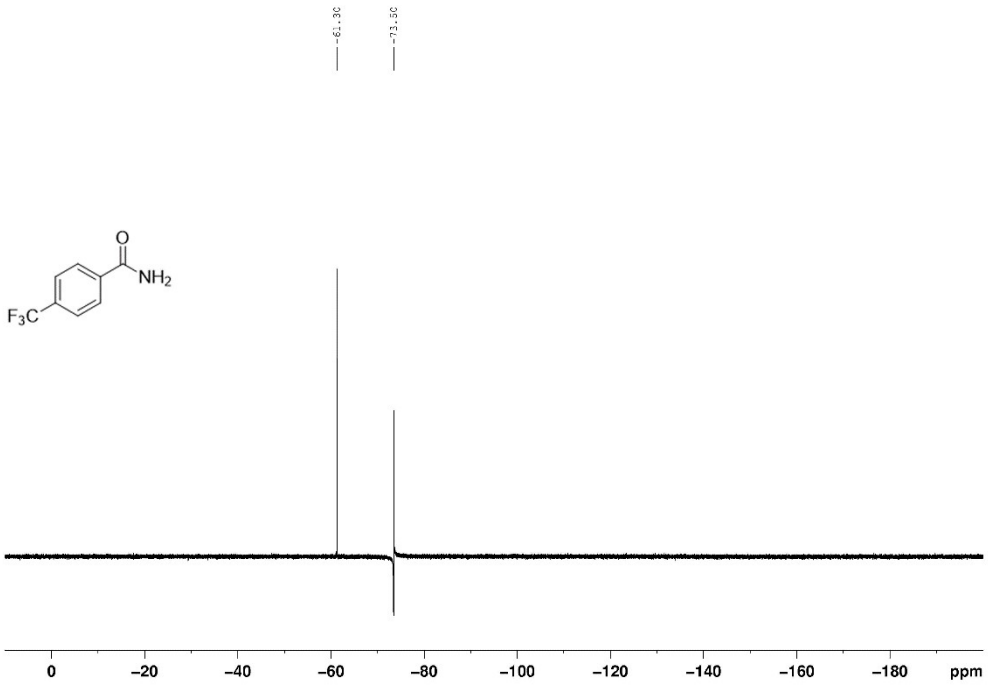
2af, ^{1}H NMR, 500 M, $CDCl_3$



2af, ^{13}C NMR, 126 M, $CDCl_3$



2af, ^{19}F NMR, 376 M, DMSO-*d6*



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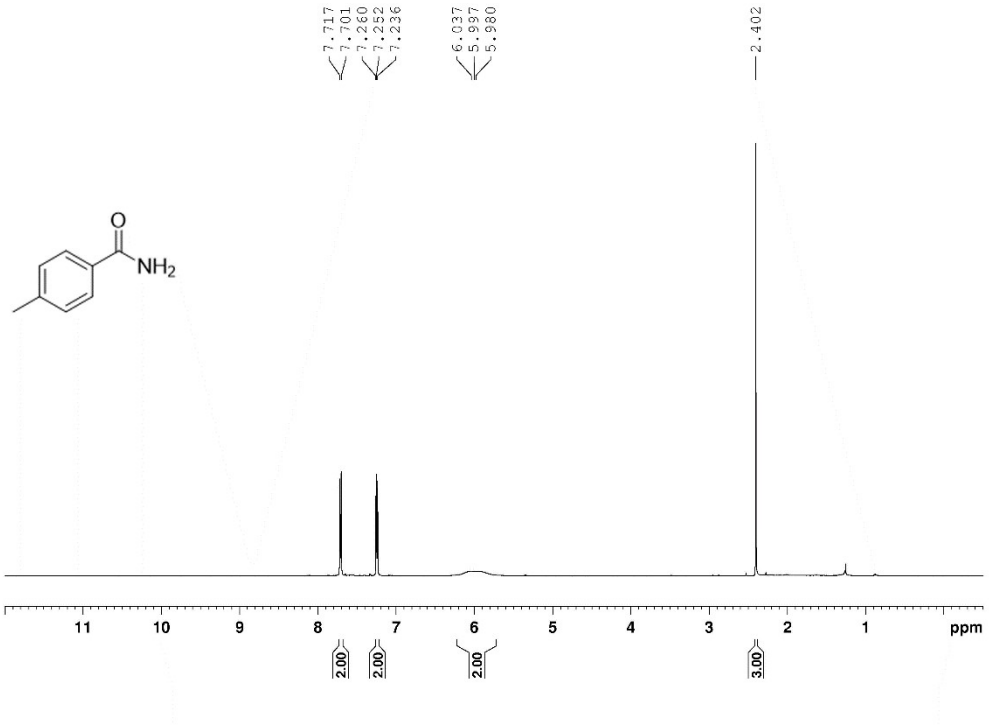
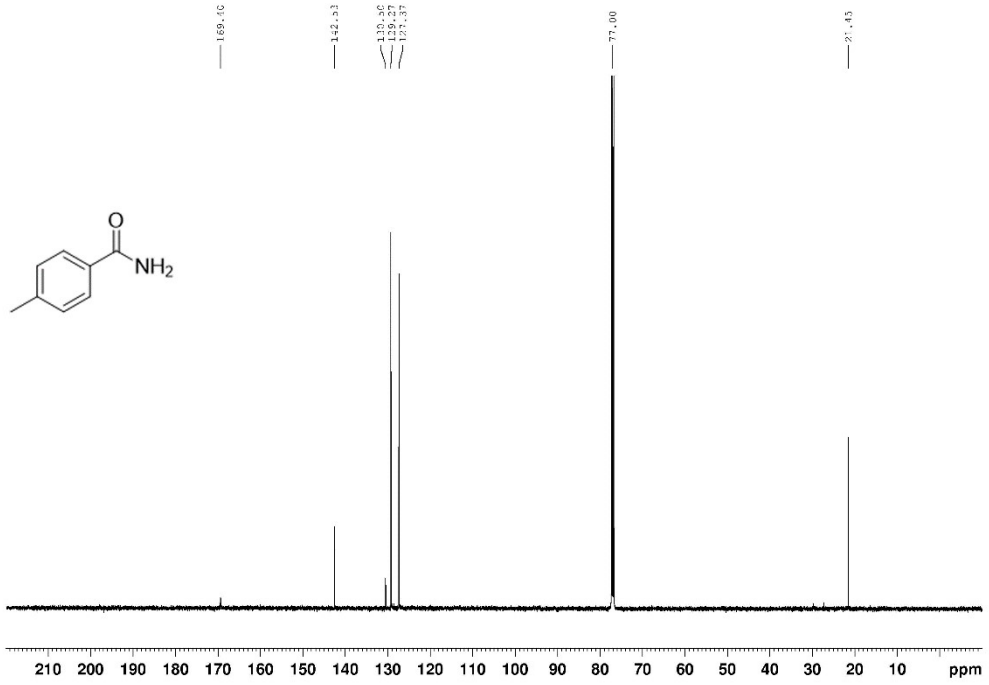
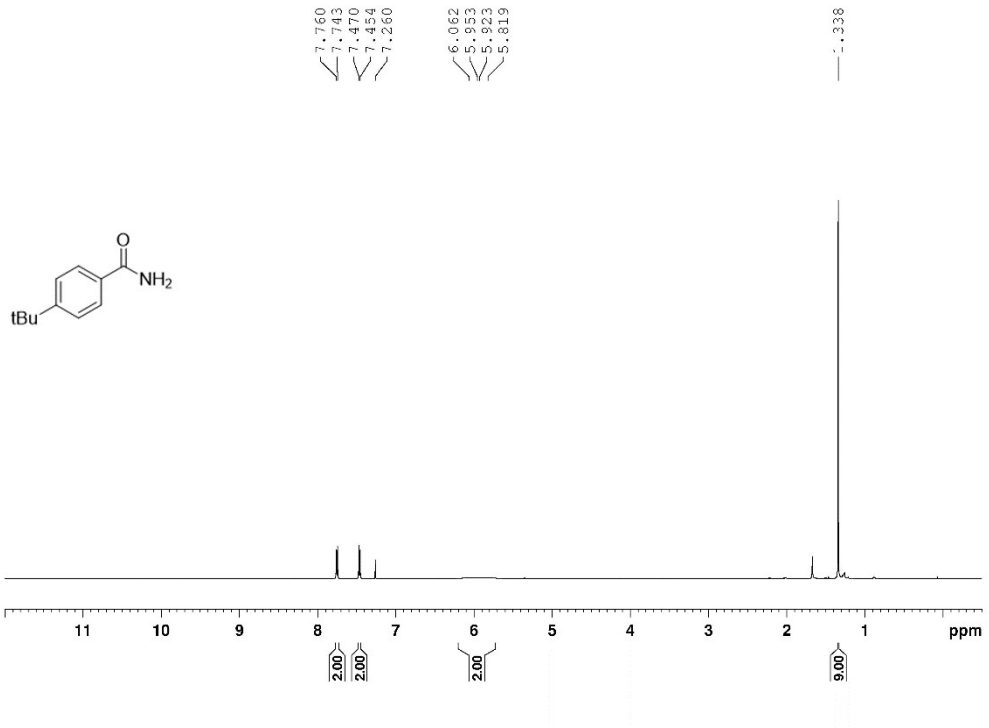


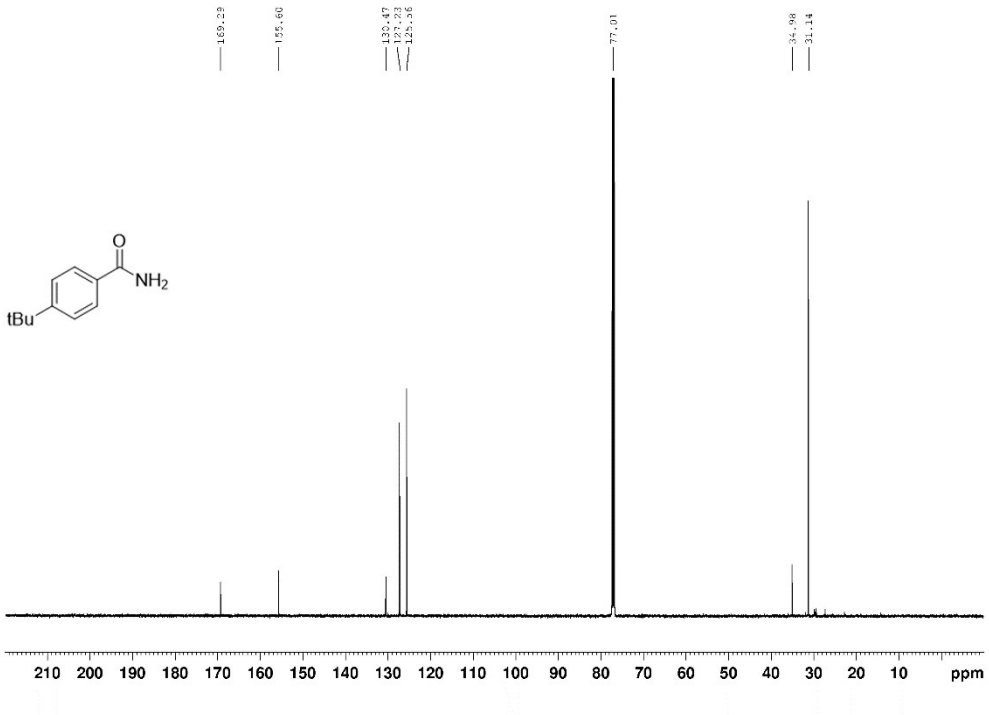
2ag, ^{13}C NMR, 126 M, $CDCl_3$



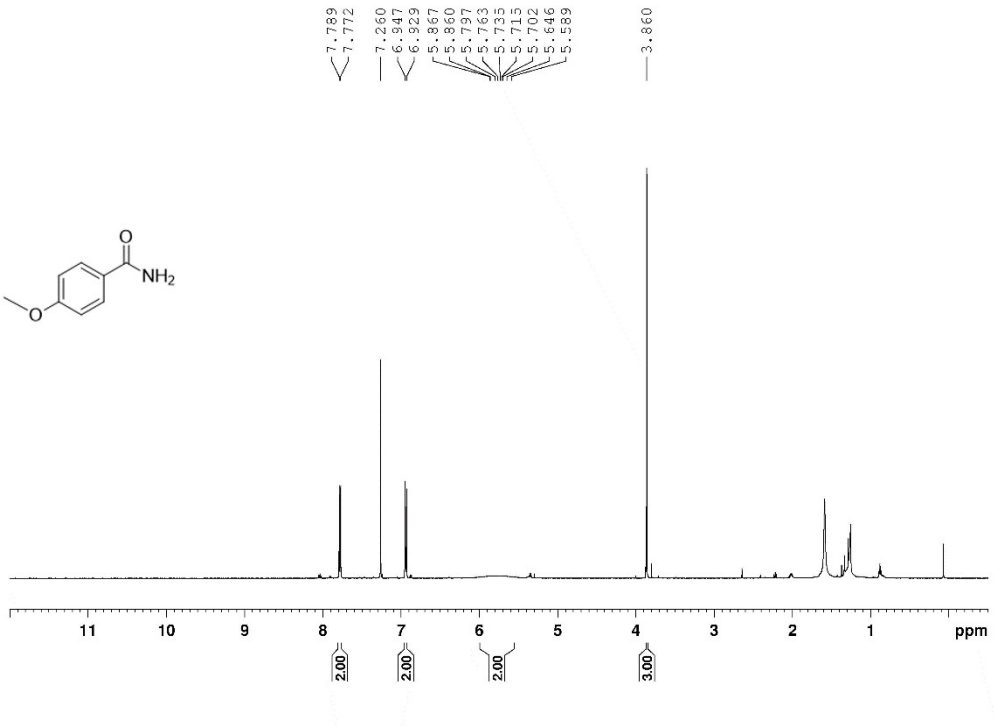
2ah, ^{1}H NMR, 500 M, $CDCl_3$



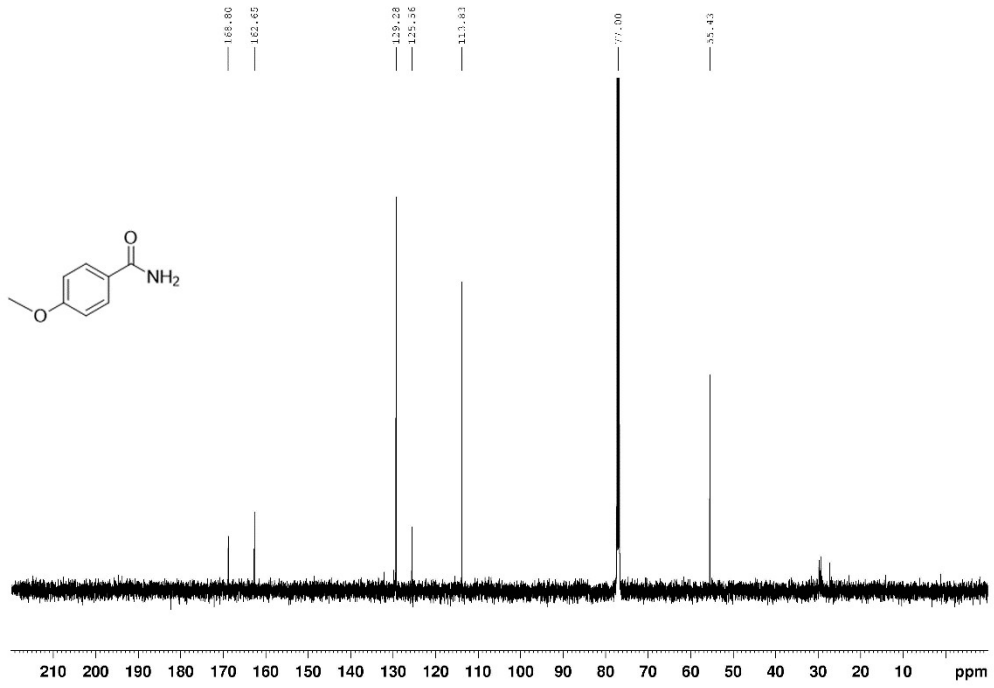
2ah, ^{13}C NMR, 126 M, $CDCl_3$



2ai, ^{1}H NMR, 500 M, $CDCl_3$



2ai, ^{13}C NMR, 126 M, $CDCl_3$



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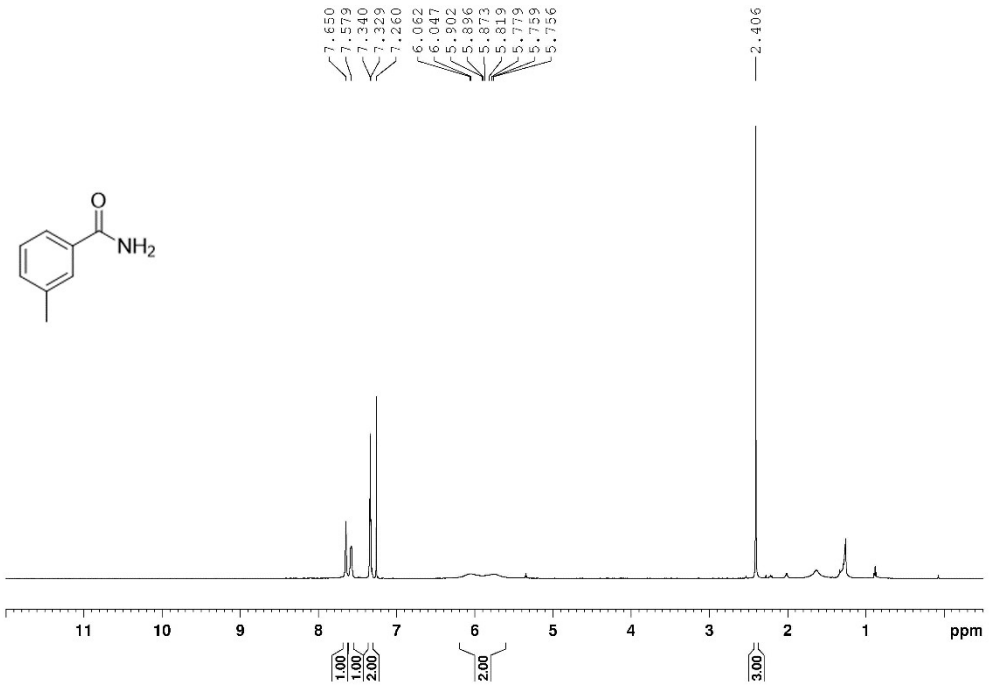
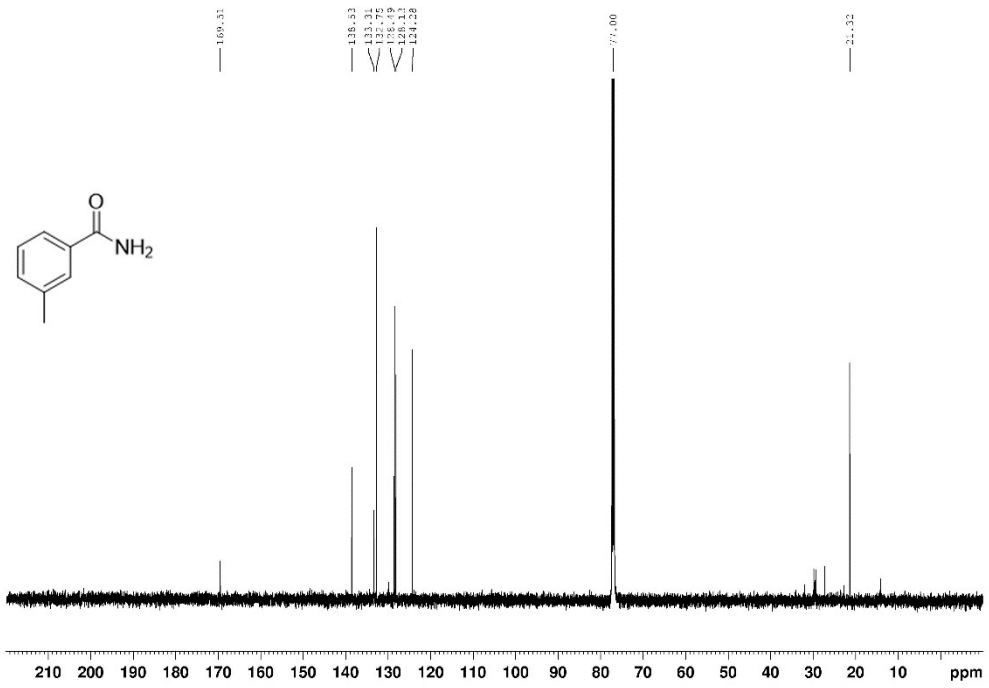
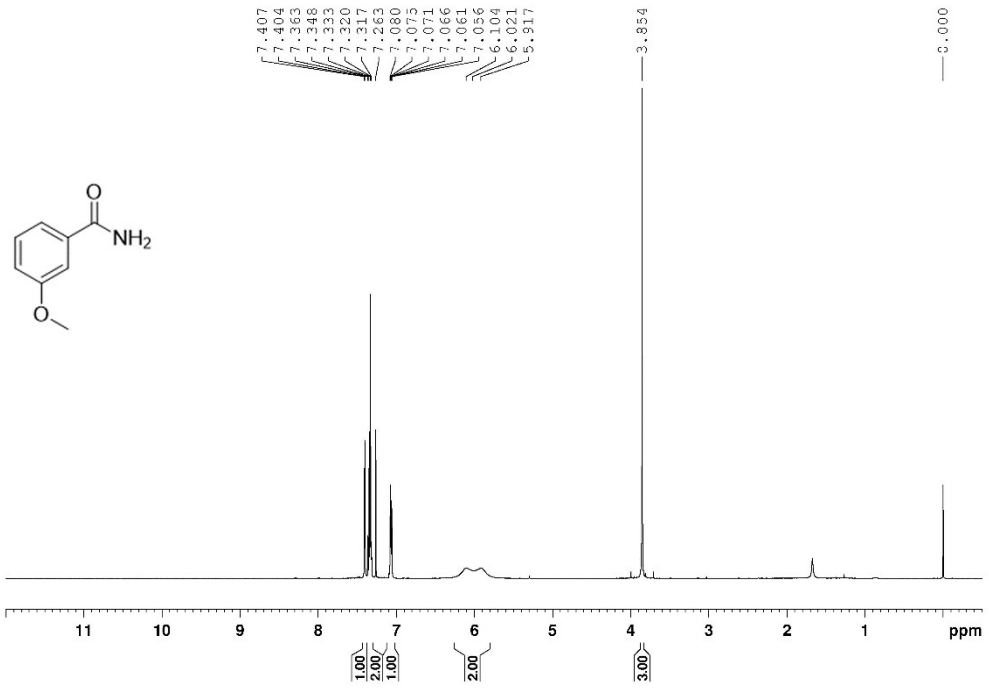


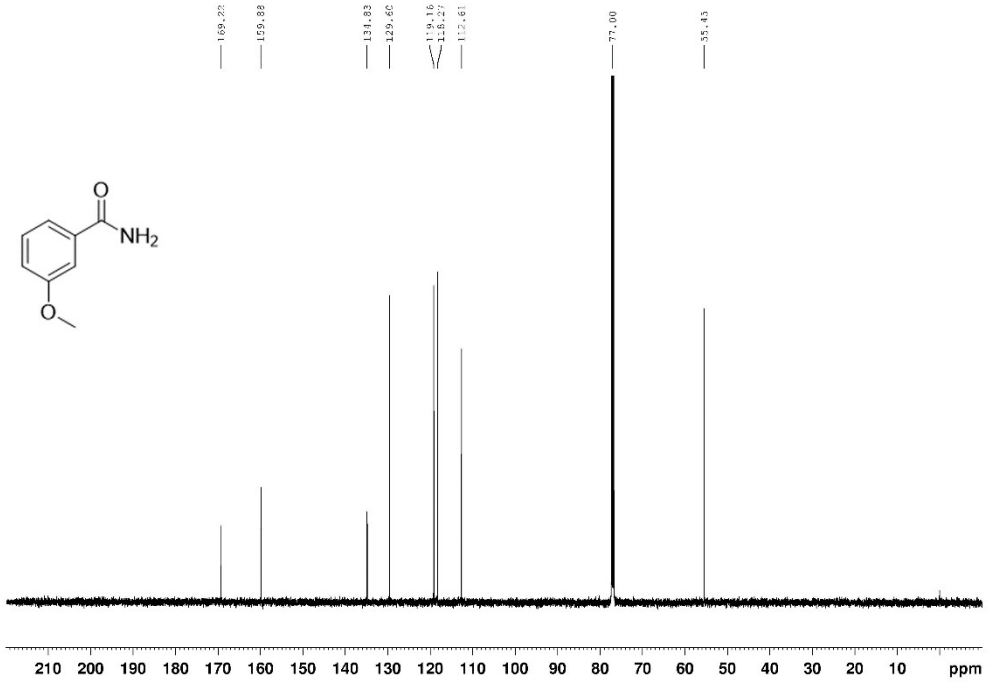
2aj, ^{13}C NMR, 126 M, $CDCl_3$



2ak, ^{1}H NMR, 500 M, $CDCl_3$



2ak, ^{13}C NMR, 126 M, $CDCl_3$



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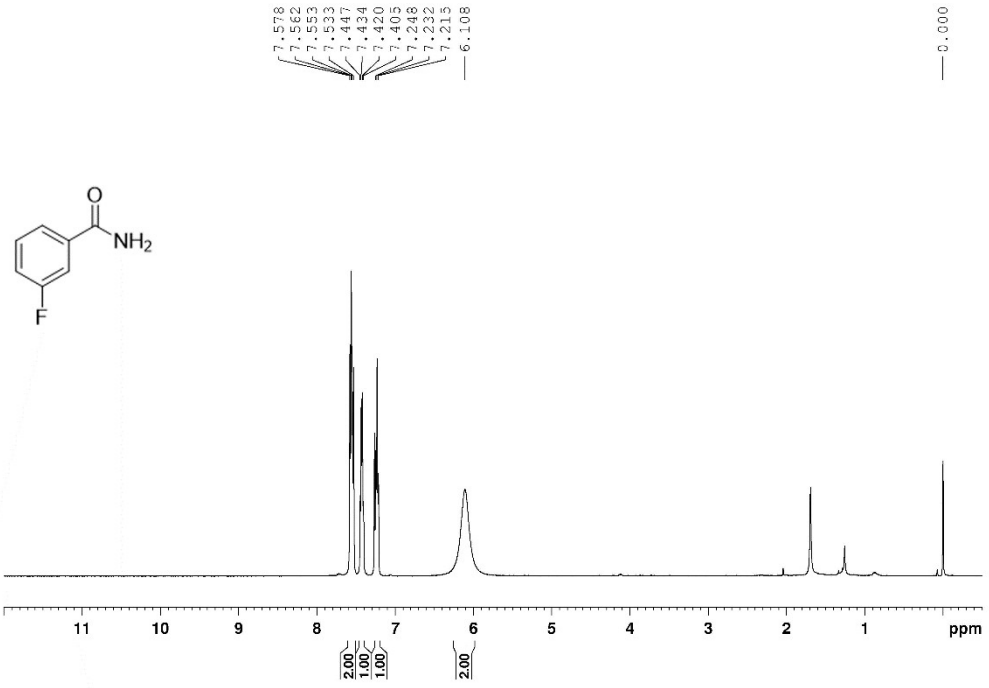
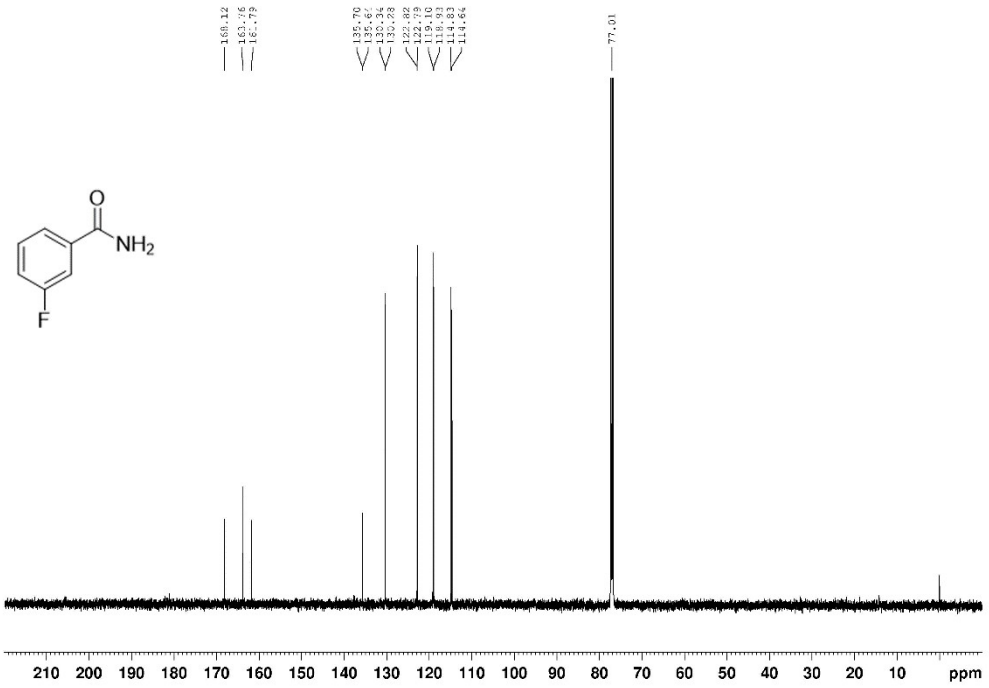
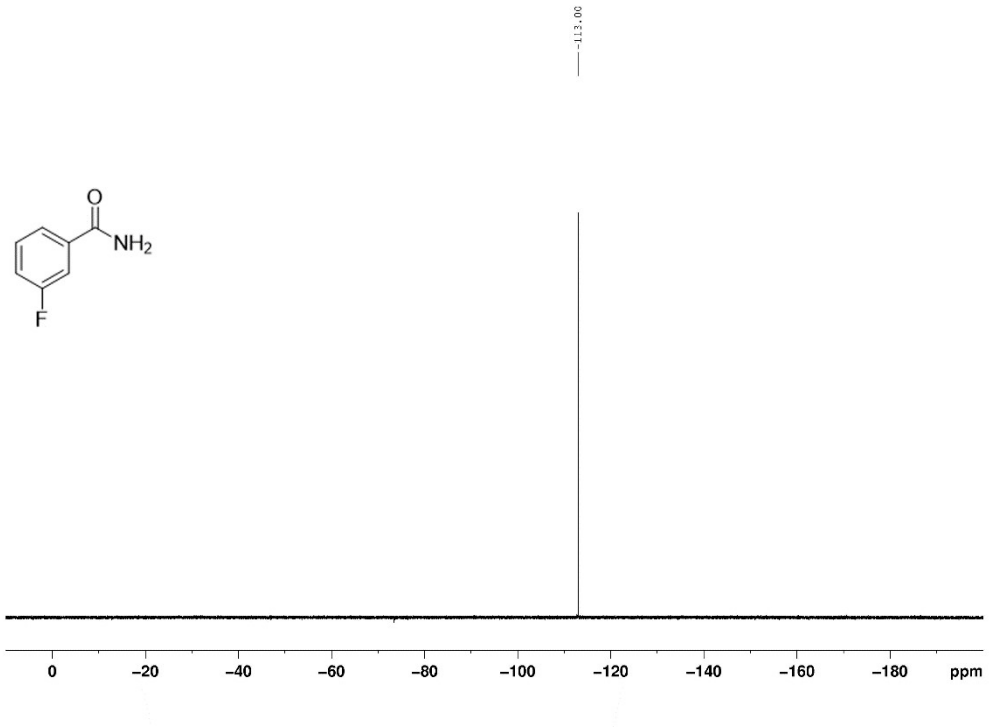


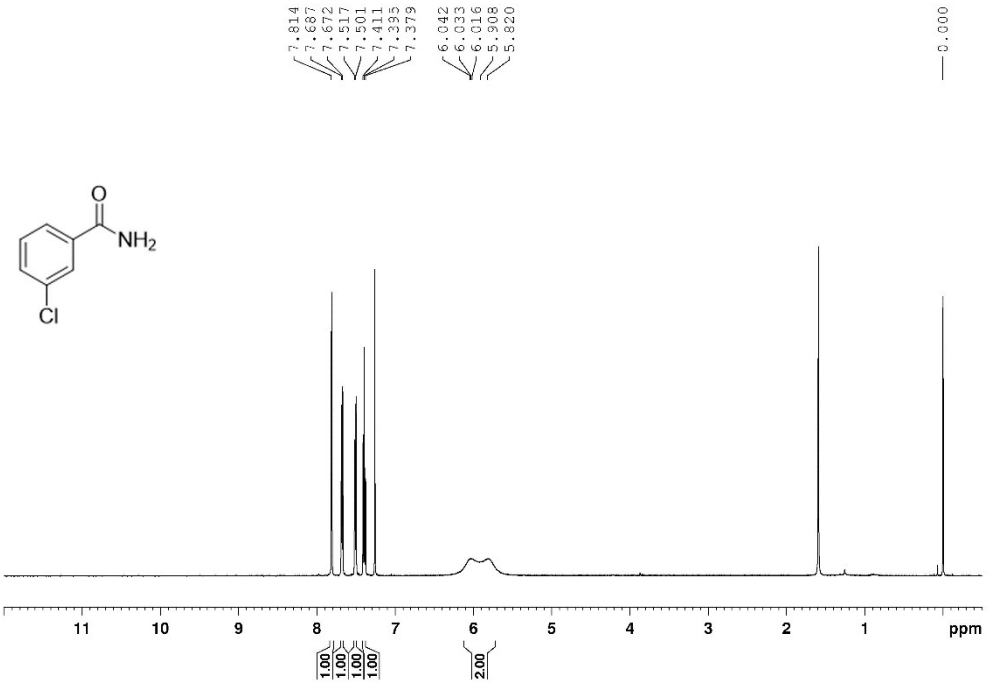
2al, ^{13}C NMR, 126 M, $CDCl_3$



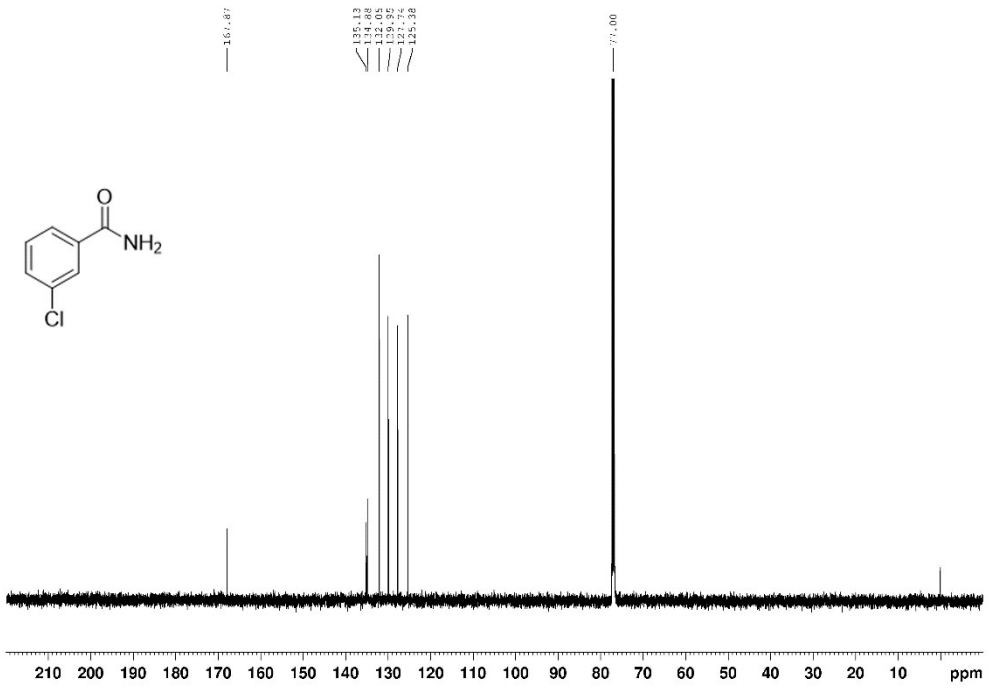
2al, ^{19}F NMR, 376 M, DMSO-*d6*



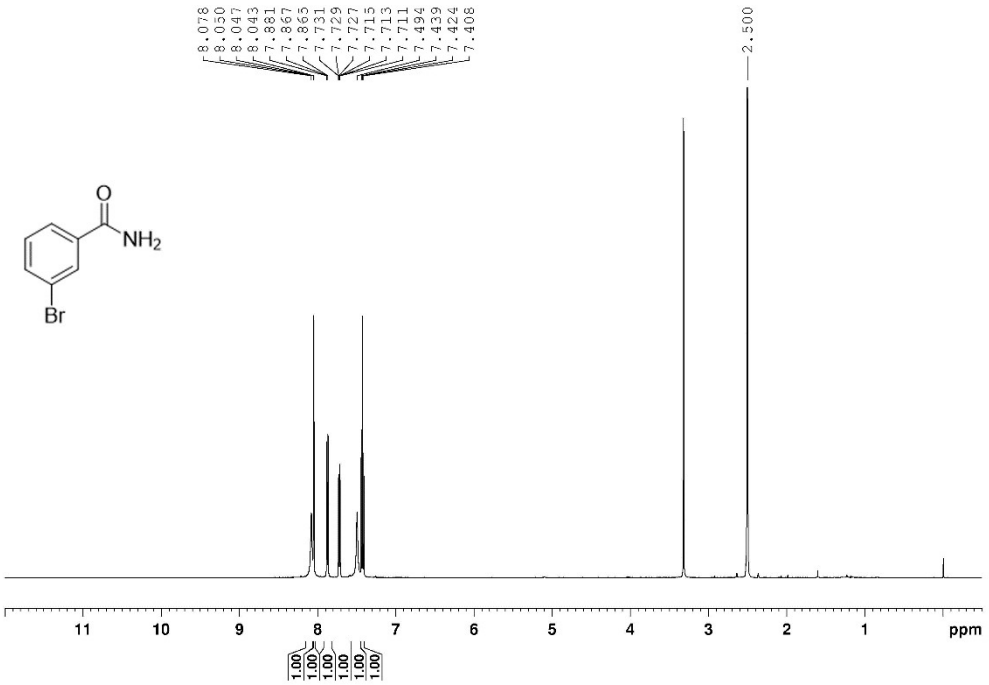
2am, ^{1}H NMR, 500 M, $CDCl_3$



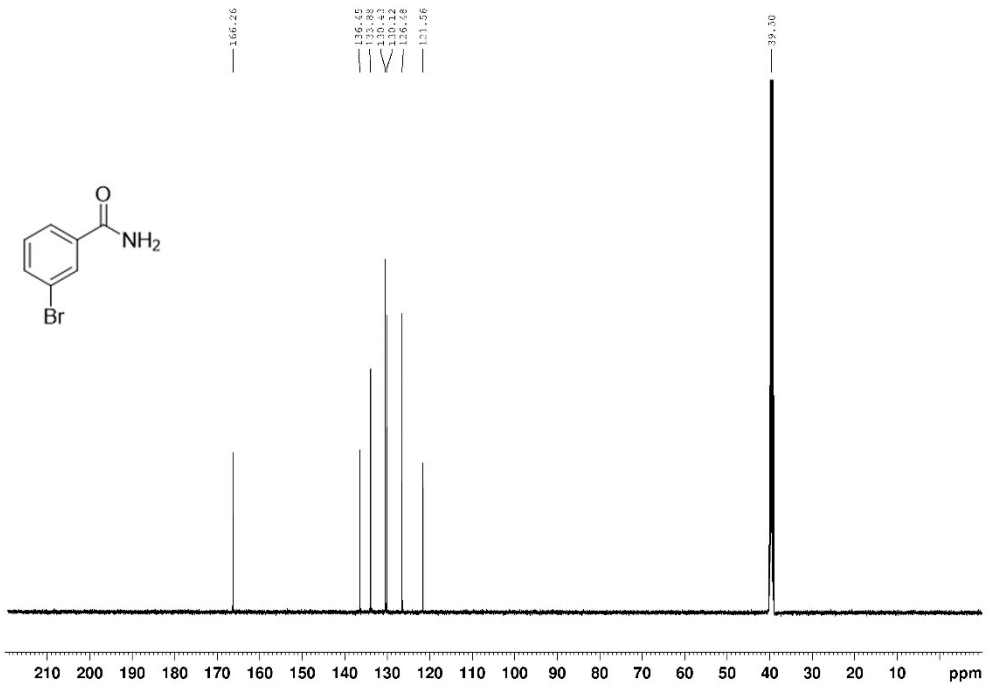
2am, ^{13}C NMR, 126 M, $CDCl_3$



2an, ^{1}H NMR, 500 M, DMSO-*d6*



2an, ^{13}C NMR, 126 M, DMSO-*d6*



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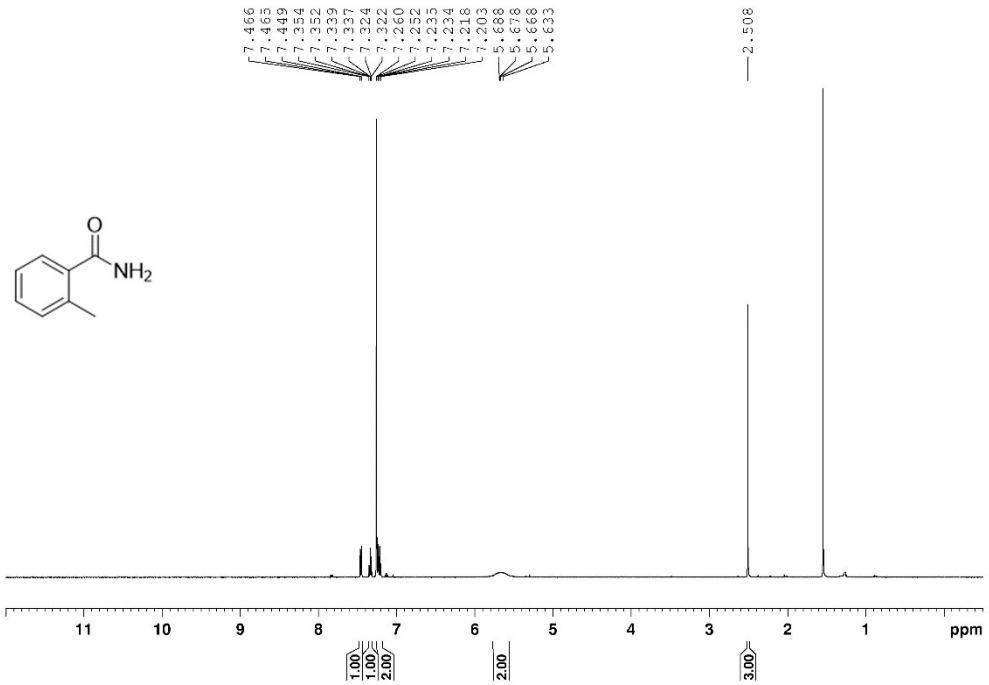

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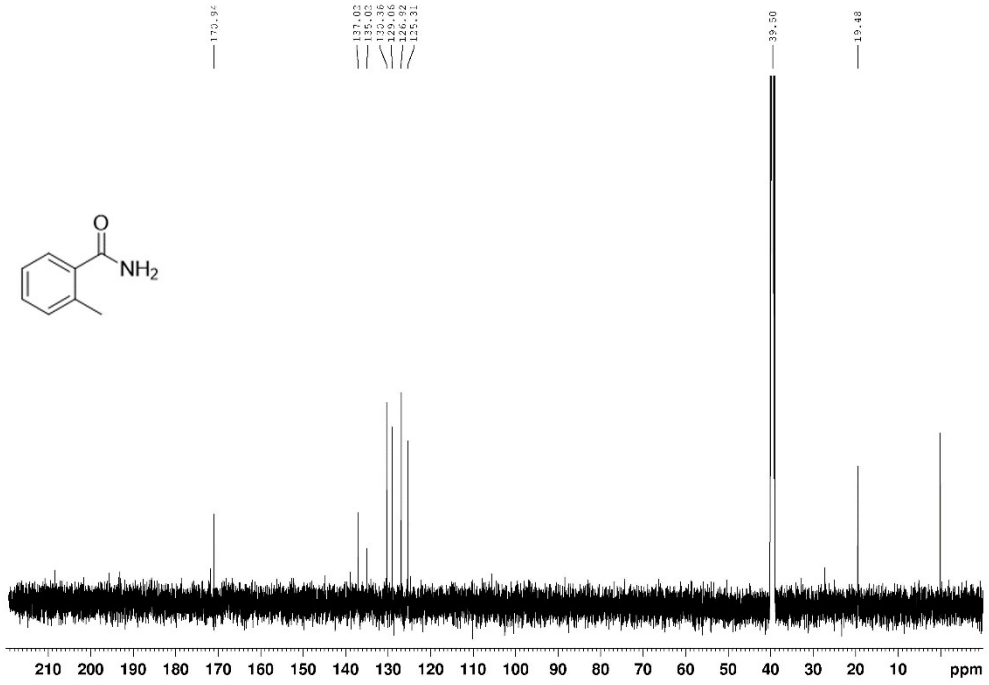
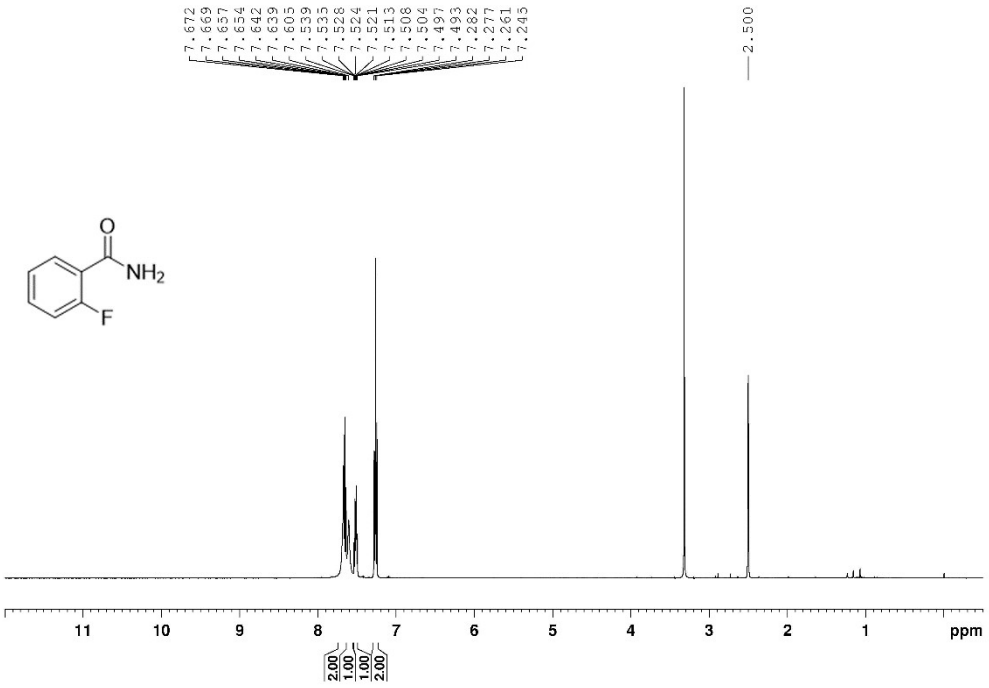
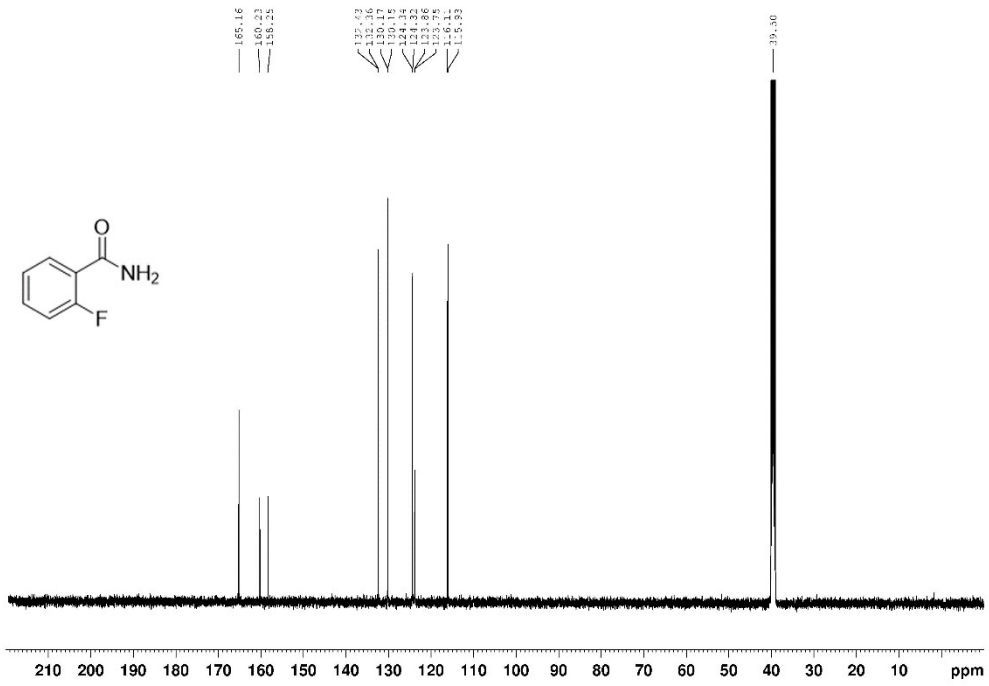


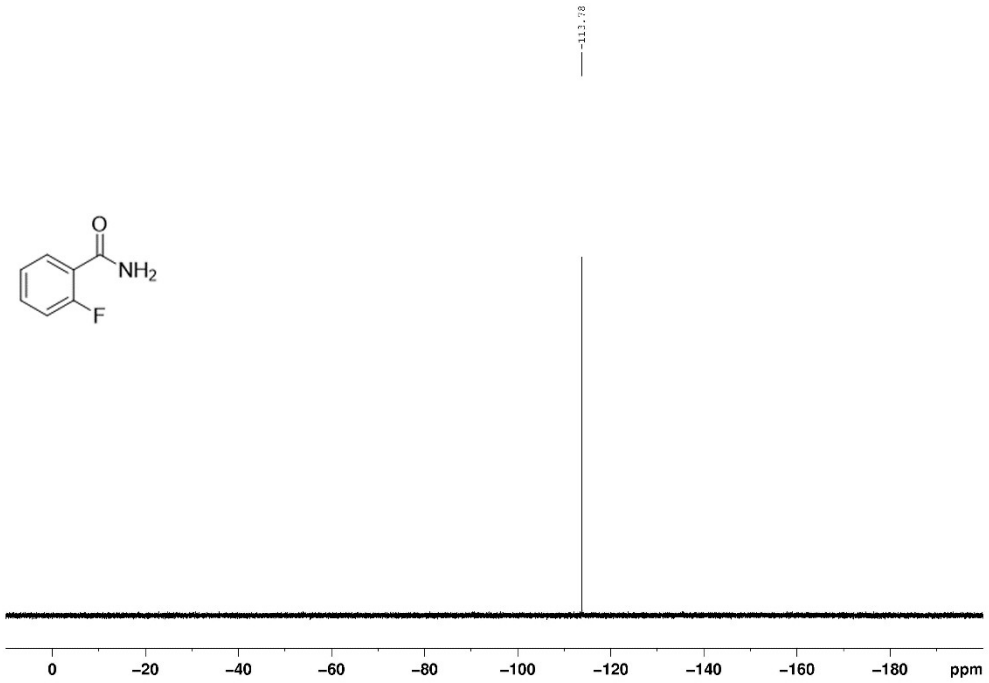
2ap, ^{1}H NMR, 500 M, DMSO-*d6*



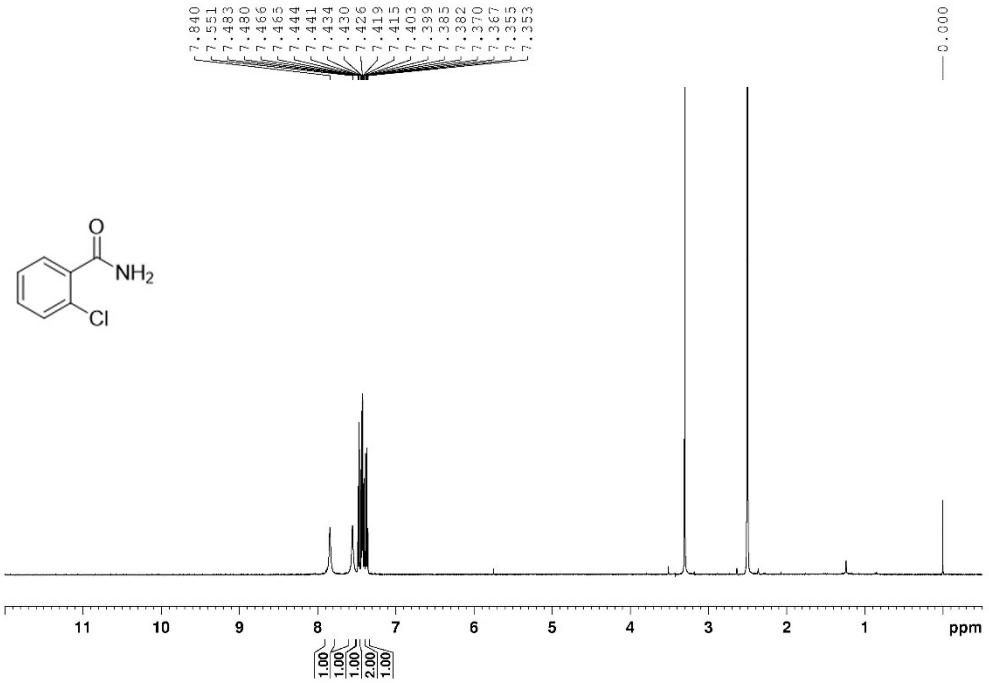
2ap, ^{13}C NMR, 126 M, DMSO-*d6*



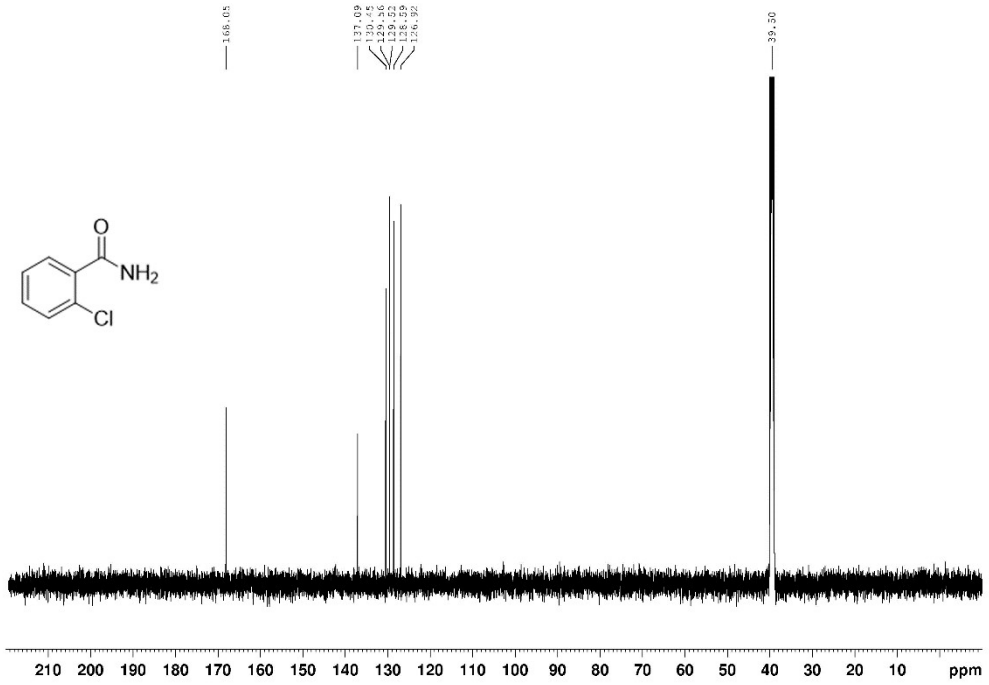
2ap, ^{19}F NMR, 376 M, DMSO-*d6*



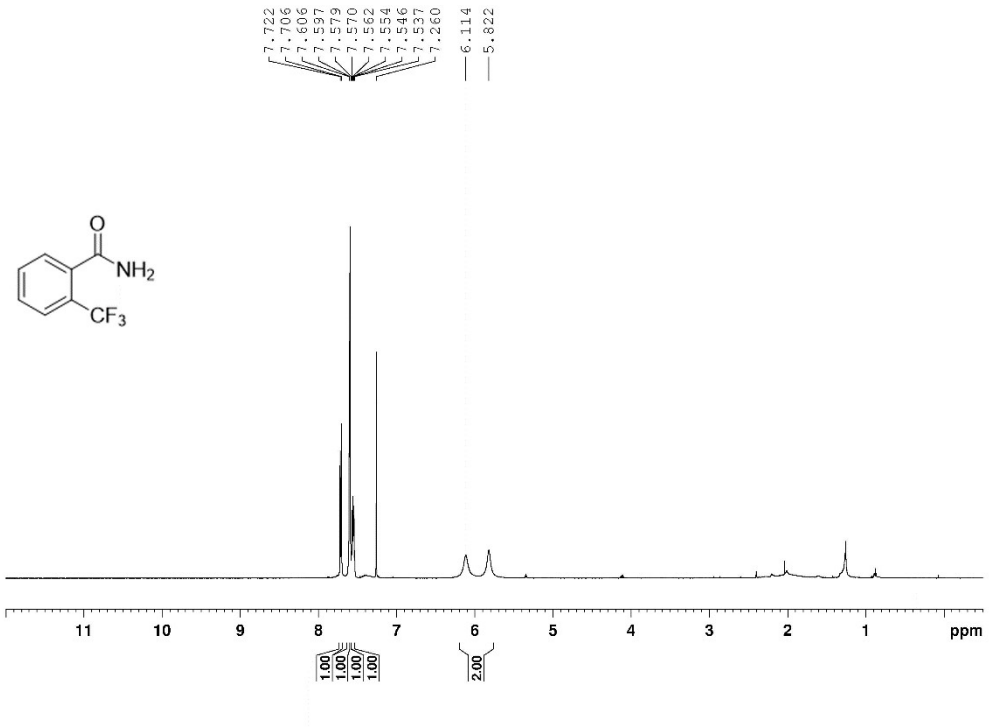
2aq, ^{1}H NMR, 500 M, DMSO-*d6*



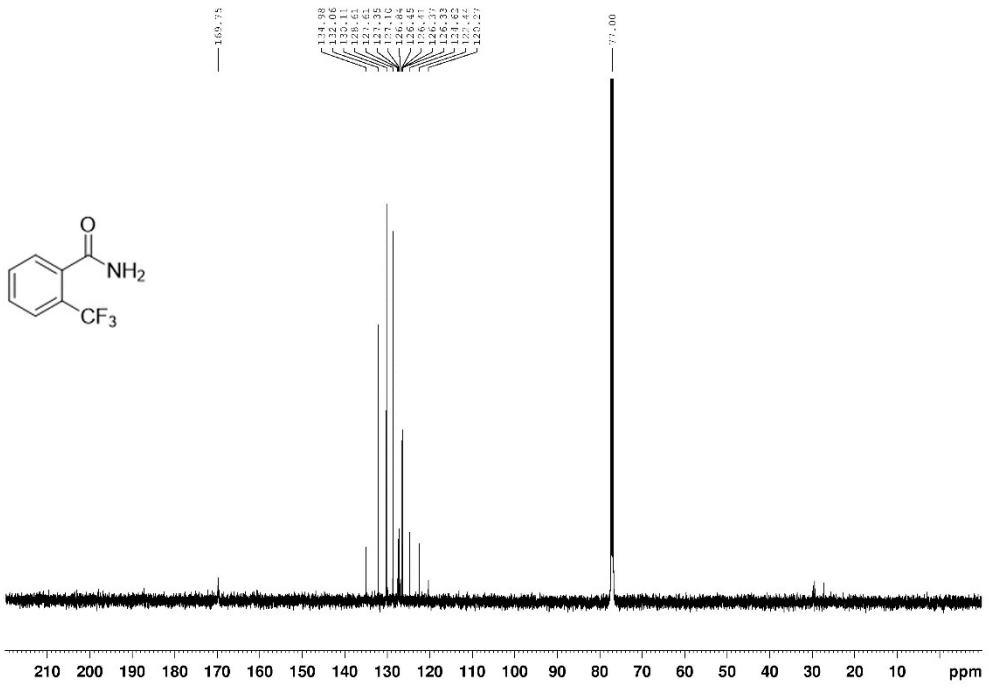
2aq, ^{13}C NMR, 126 M, DMSO-*d6*



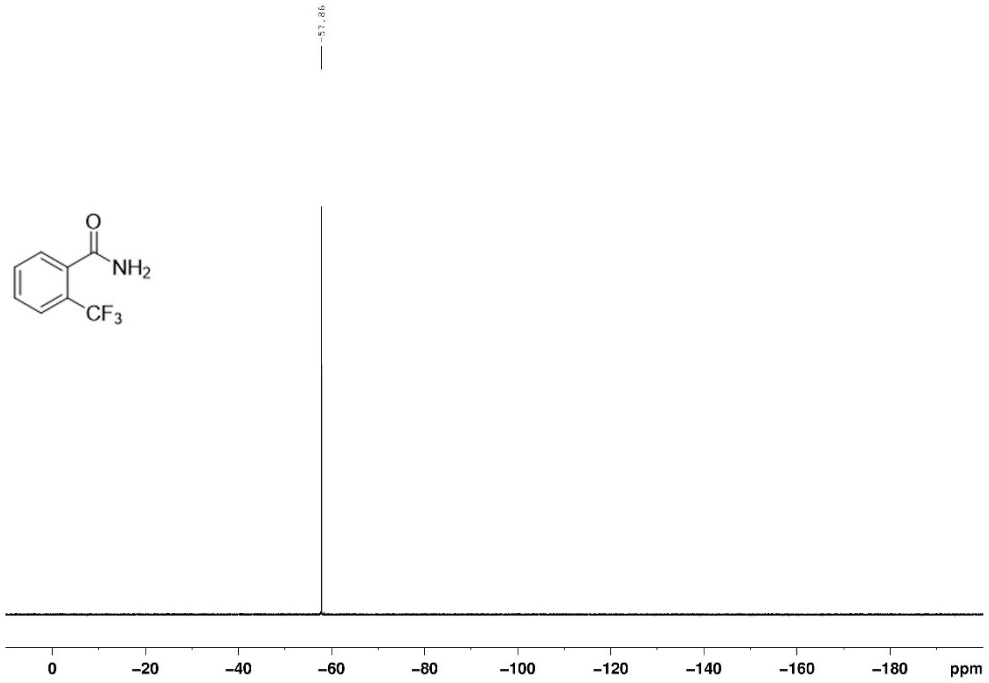
2ar, ^{1}H NMR, 500 M, $CDCl_3$



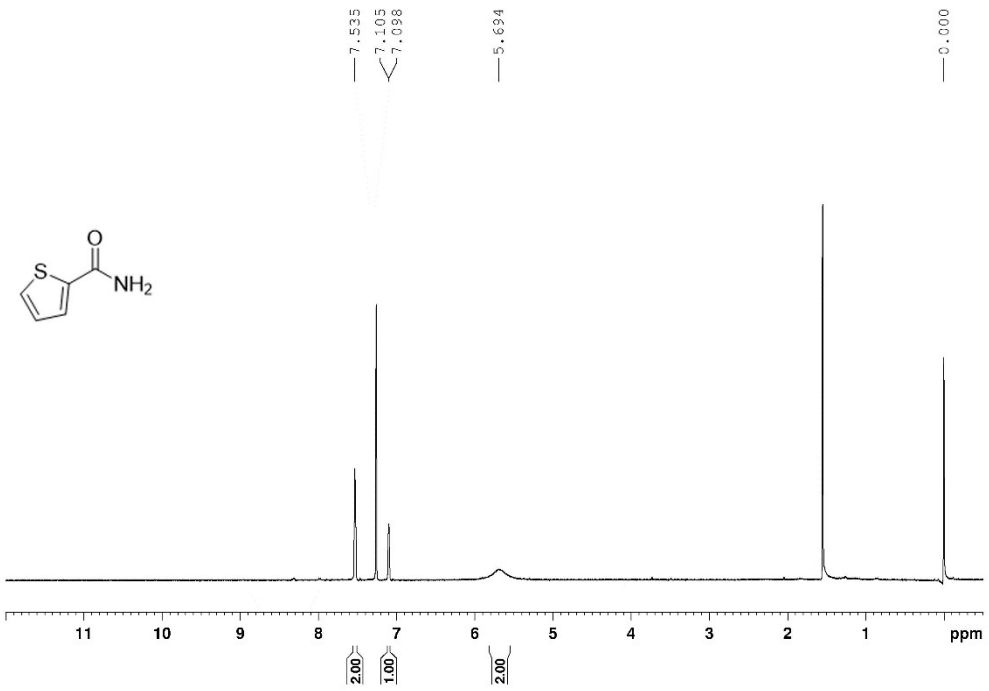
2ar, ^{13}C NMR, 126 M, $CDCl_3$



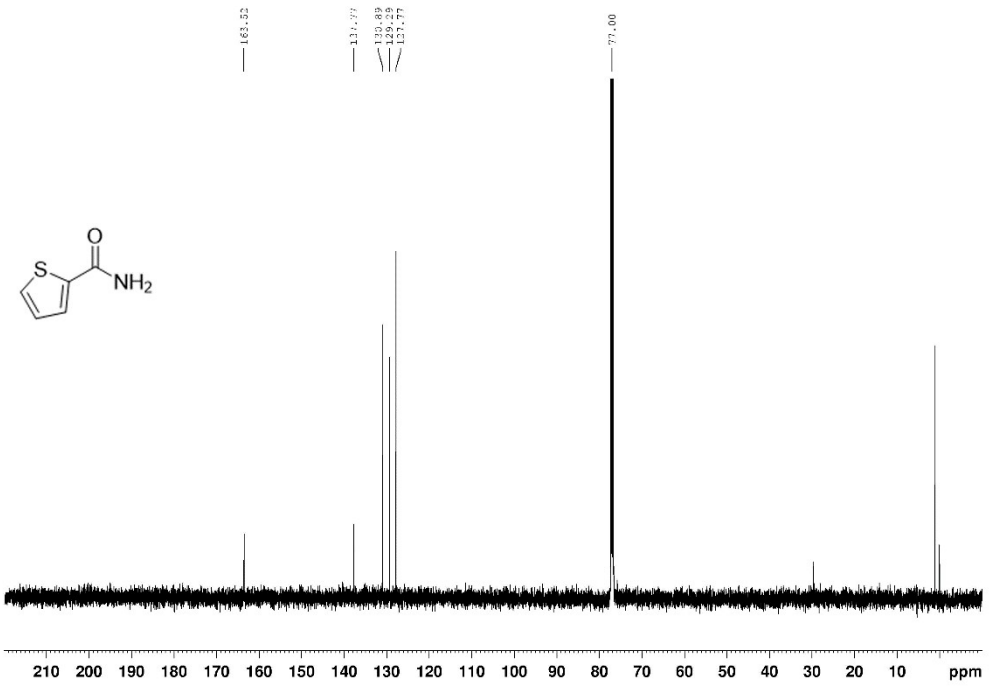
2ar, ^{19}F NMR, 376 M, DMSO-*d6*



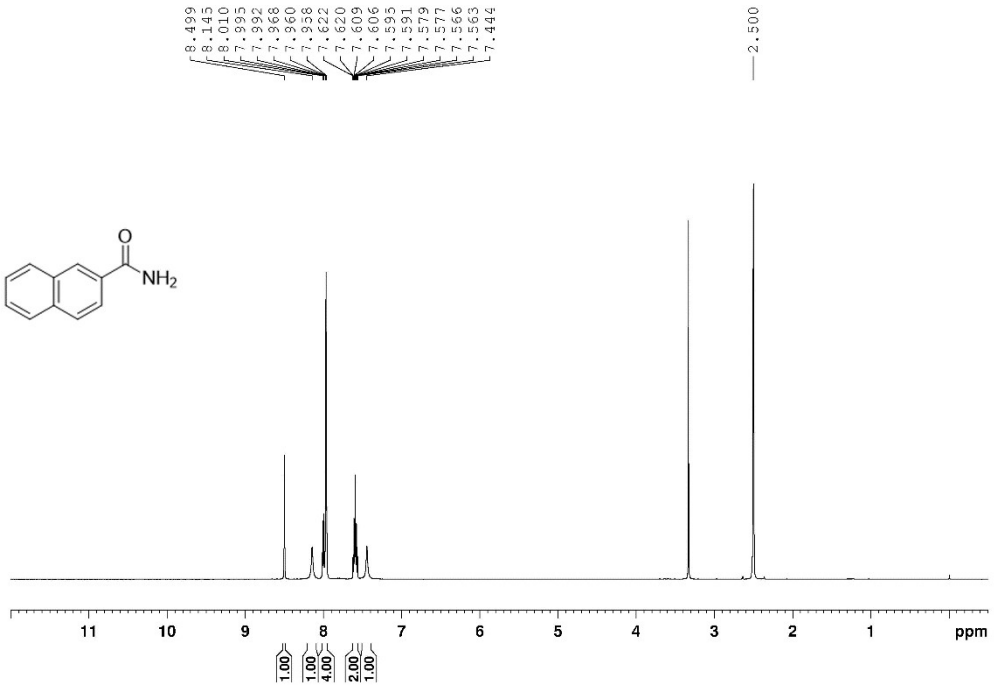
2as, ^{1}H NMR, 500 M, $CDCl_3$



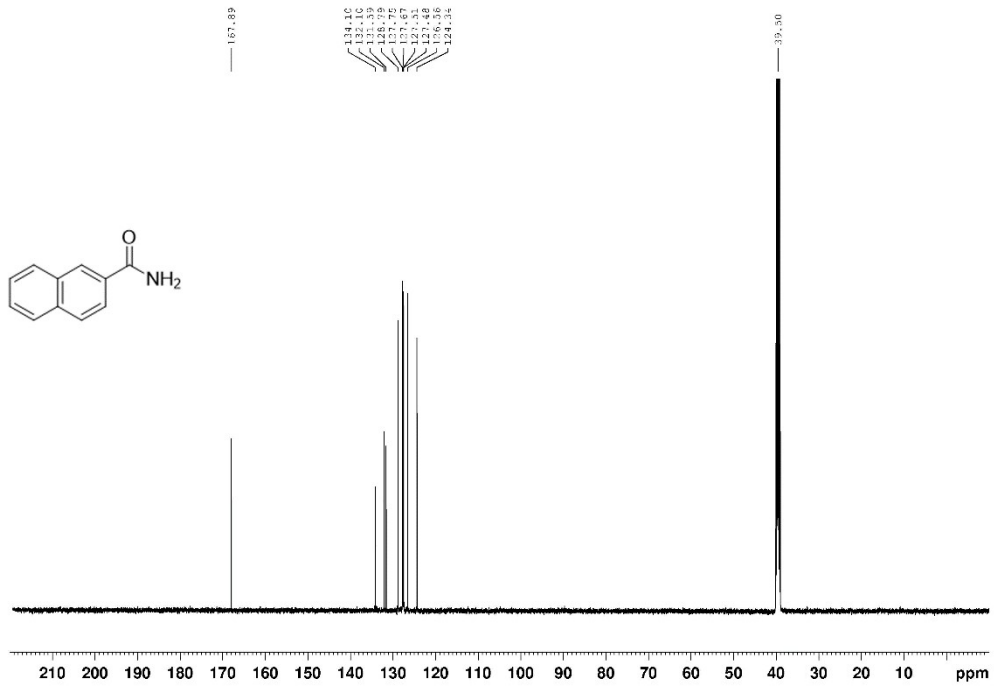
2as, ^{13}C NMR, 126 M, $CDCl_3$



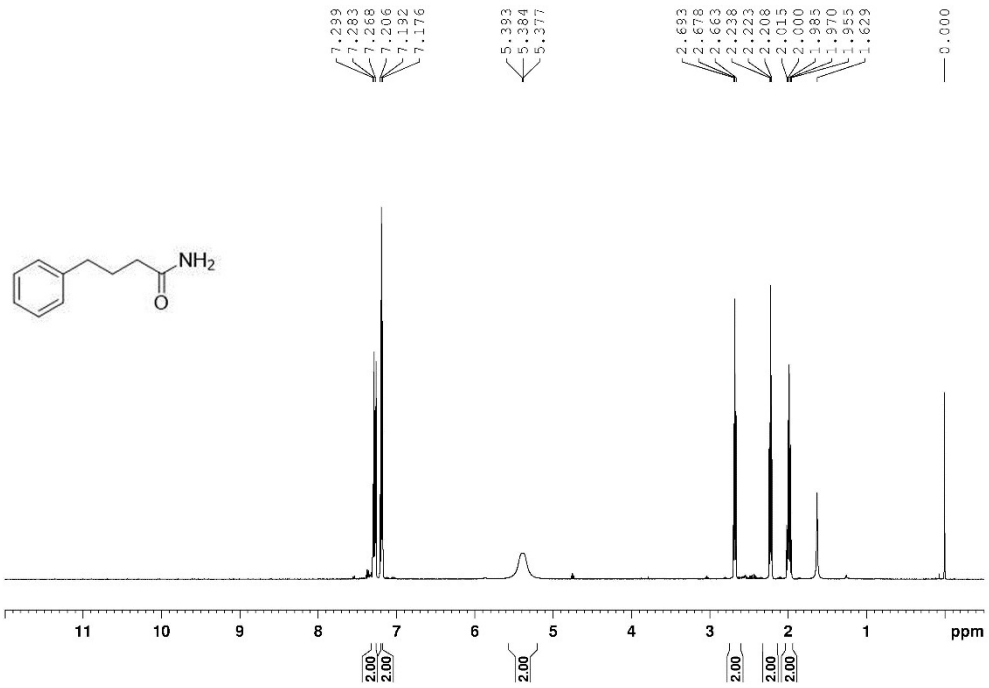
2at, ^{1}H NMR, 500 M, $CDCl_3$



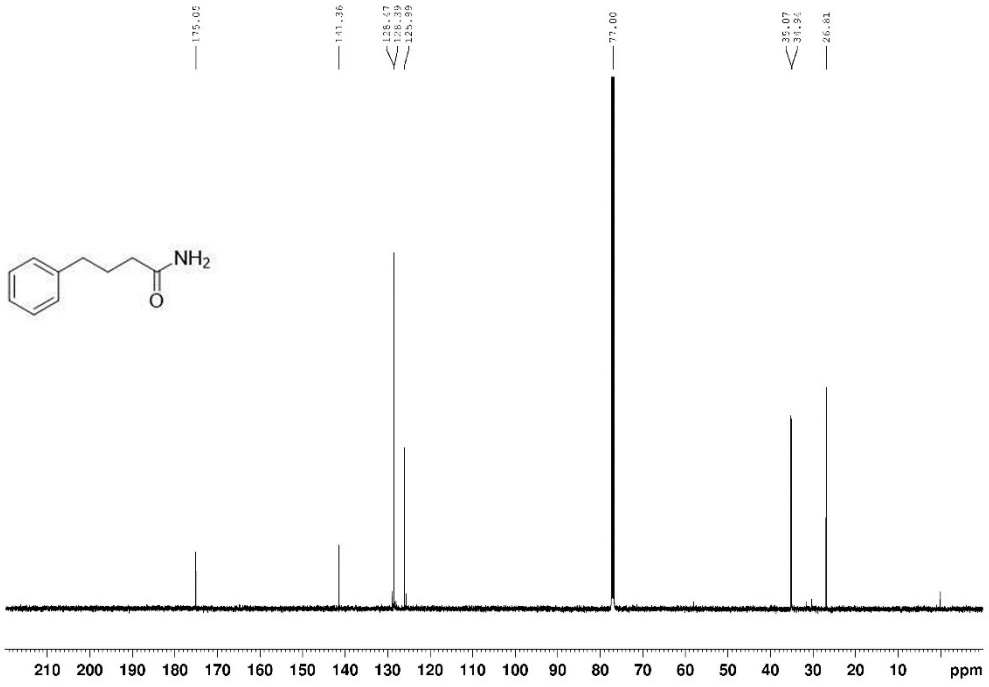
2at, ^{13}C NMR, 126 M, $CDCl_3$



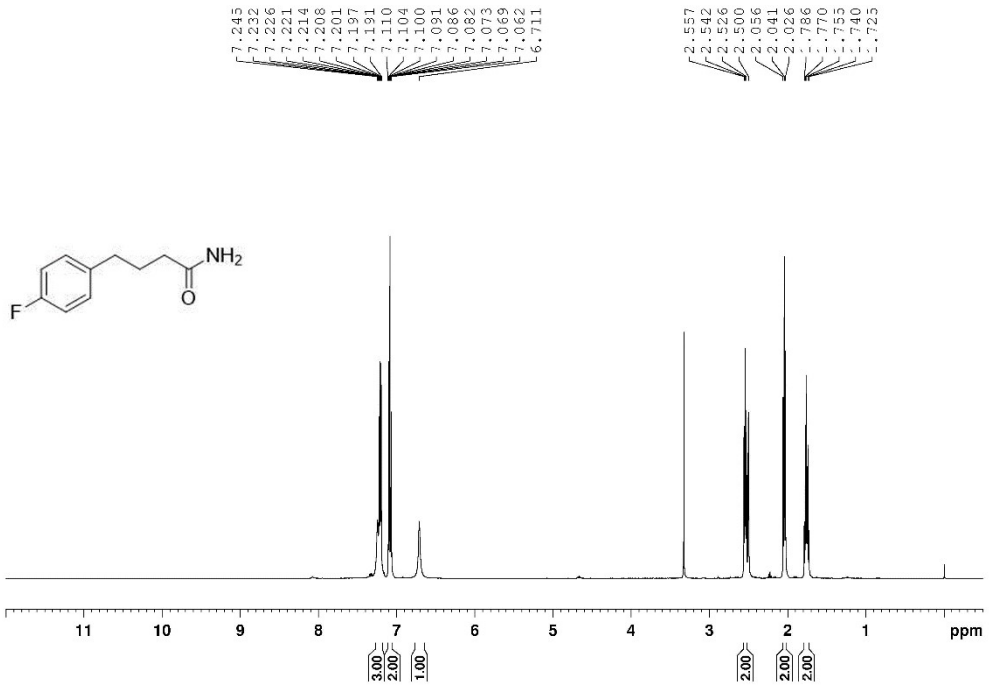
4aa, ^{1}H NMR, 500 M, DMSO-*d6*



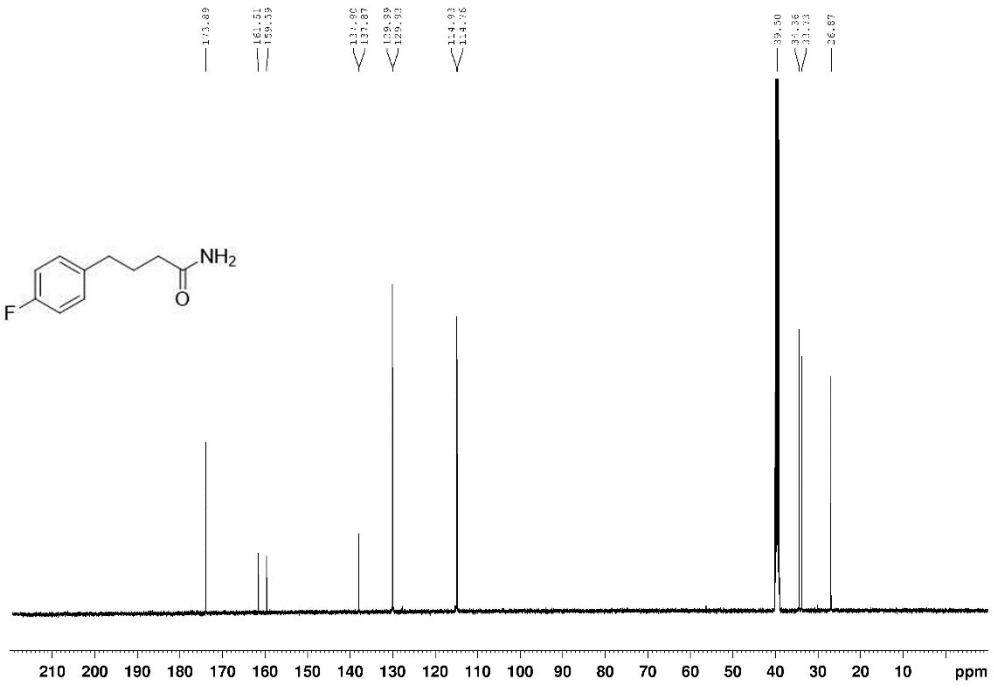
4aa, ^{13}C NMR, 126 M, DMSO-*d6*



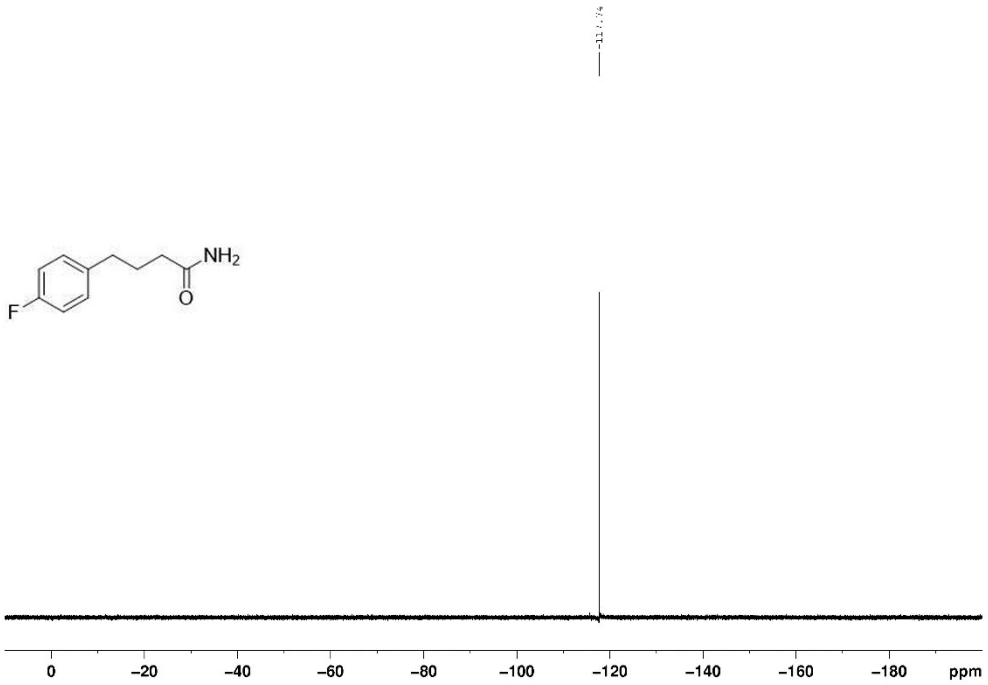
4ab, ^{1}H NMR, 500 M, DMSO-*d6*



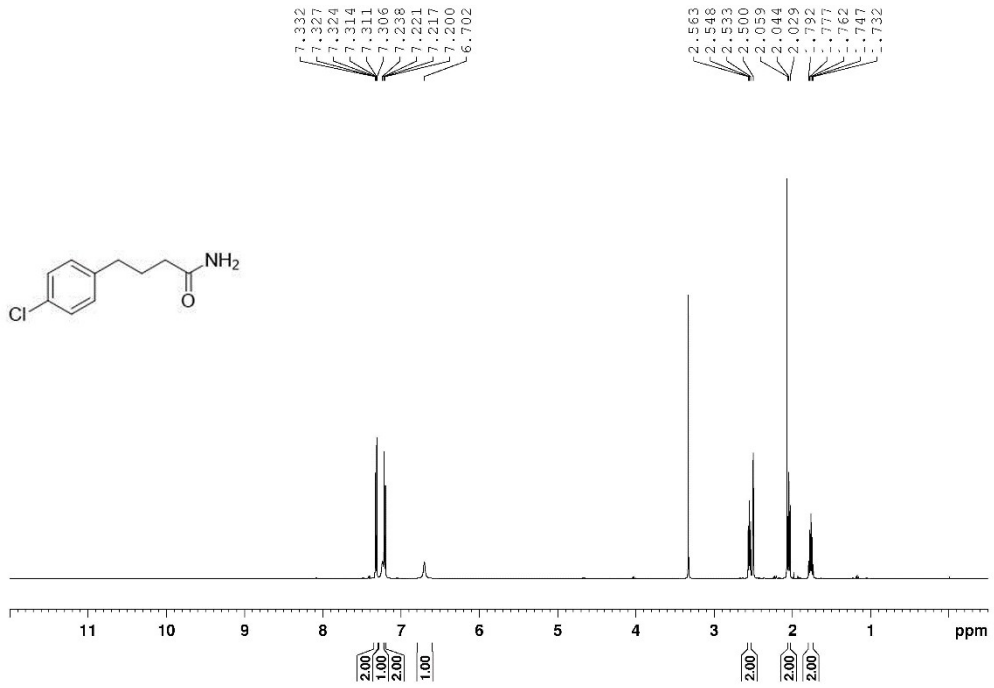
4ab, ^{13}C NMR, 126 M, DMSO-*d6*



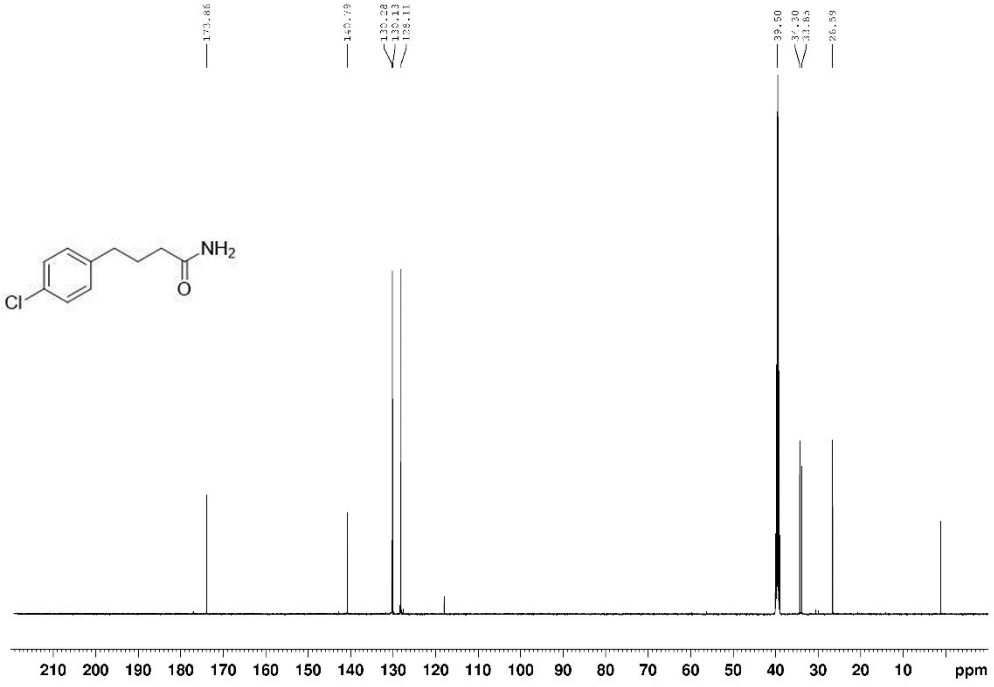
4ab, ^{19}F NMR, 376 M, DMSO-*d6*



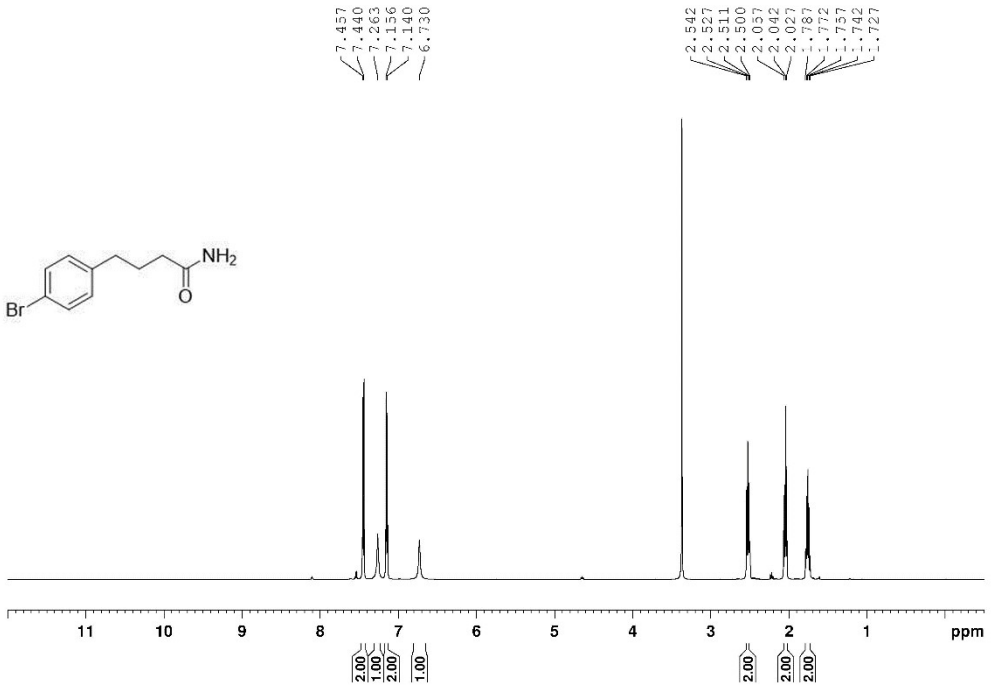
4ac, ^{1}H NMR, 500 M, DMSO-*d6*



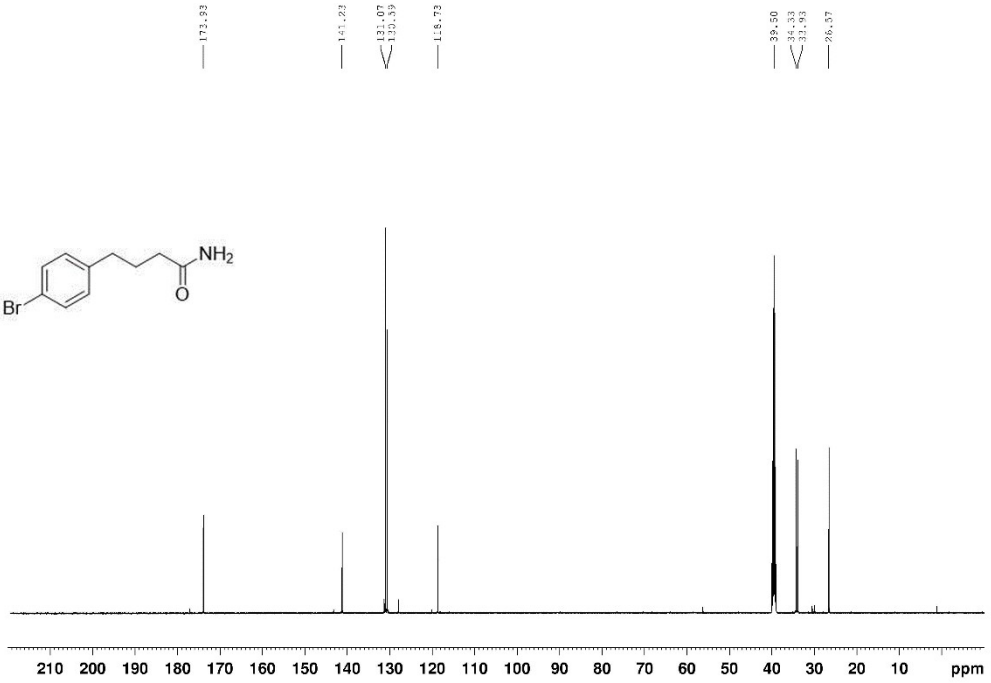
4ac, ^{13}C NMR, 126 M, DMSO-*d6*



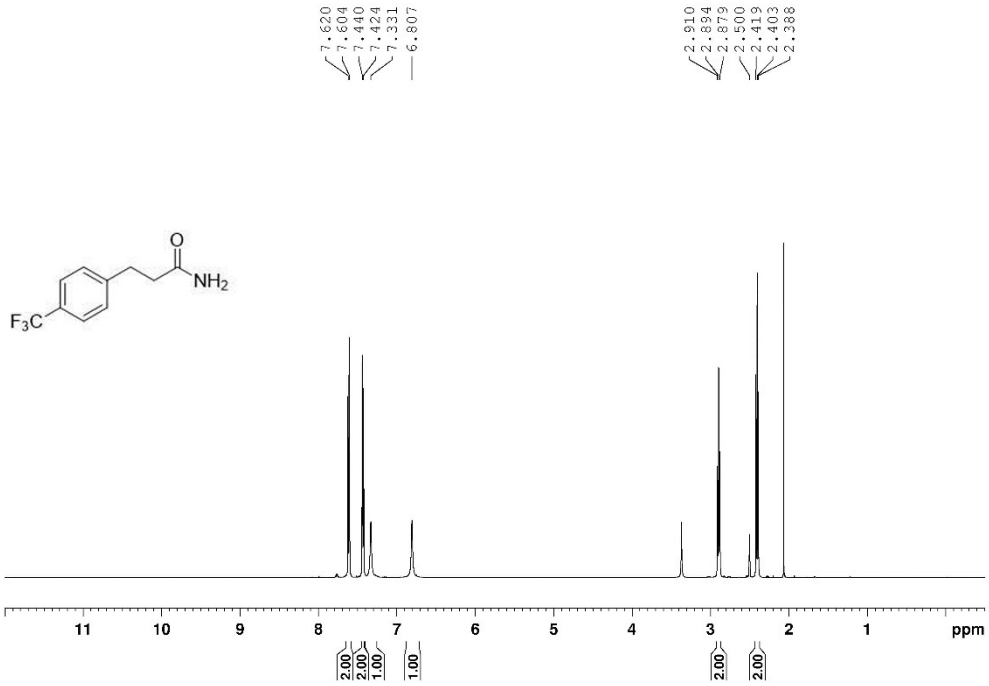
4ad, ^{1}H NMR, 500 M, DMSO-*d6*



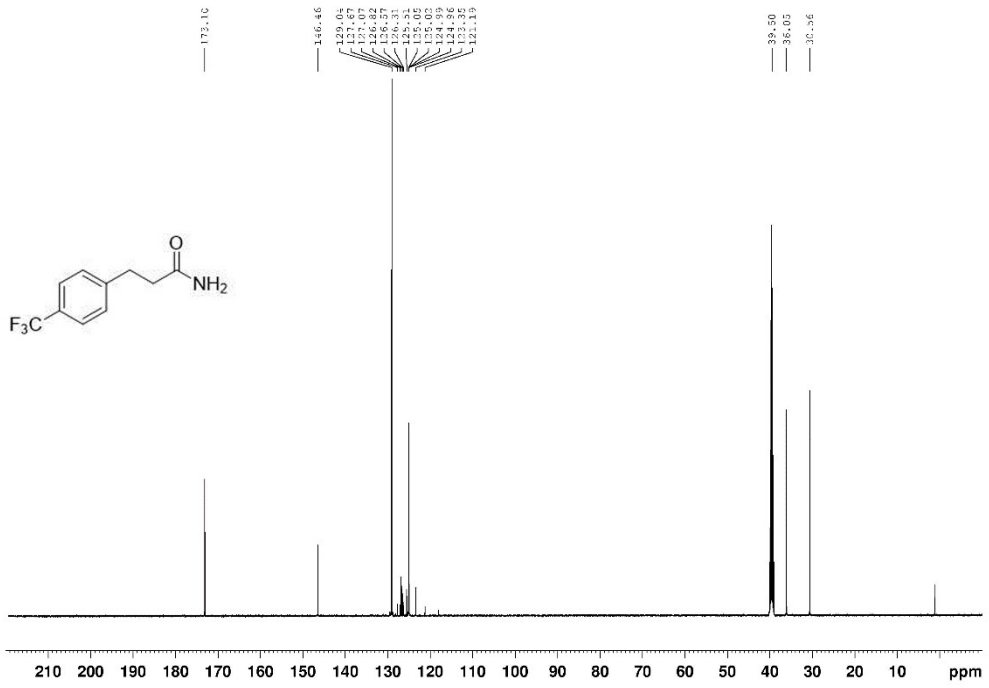
4ad, ^{13}C NMR, 126 M, DMSO-*d6*



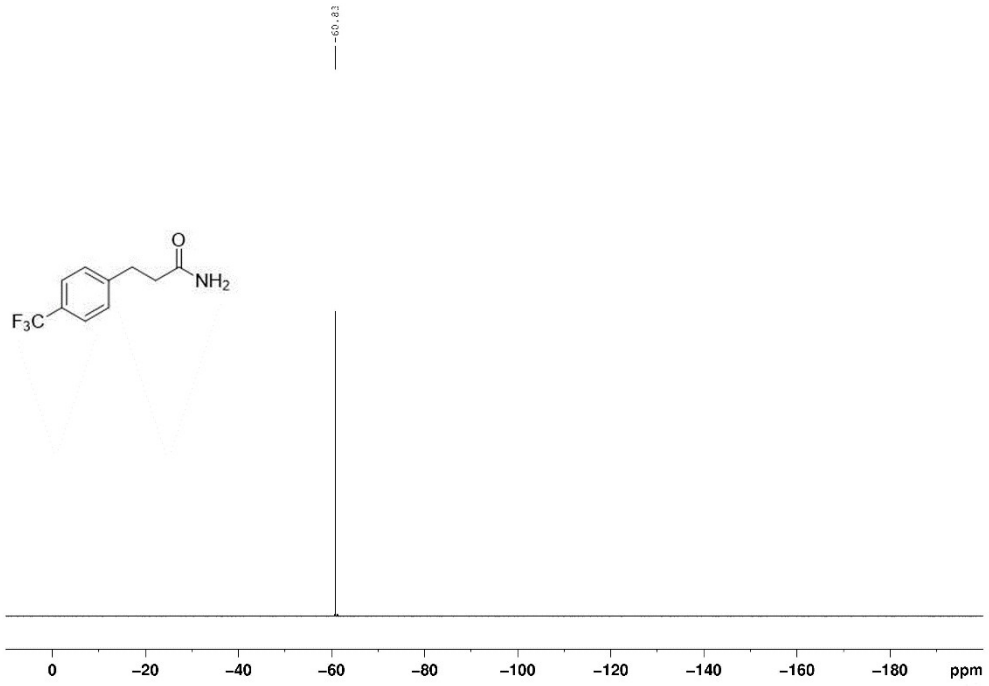
4ae, ^{1}H NMR, 500 M, DMSO-*d6*



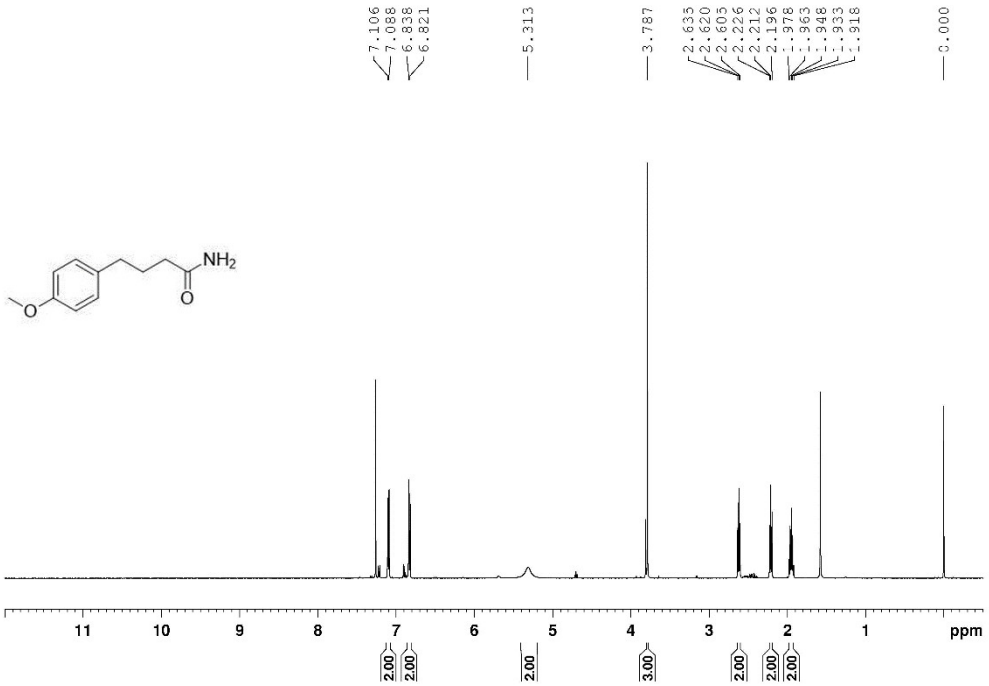
4ae, ^{13}C NMR, 126 M, DMSO-*d6*



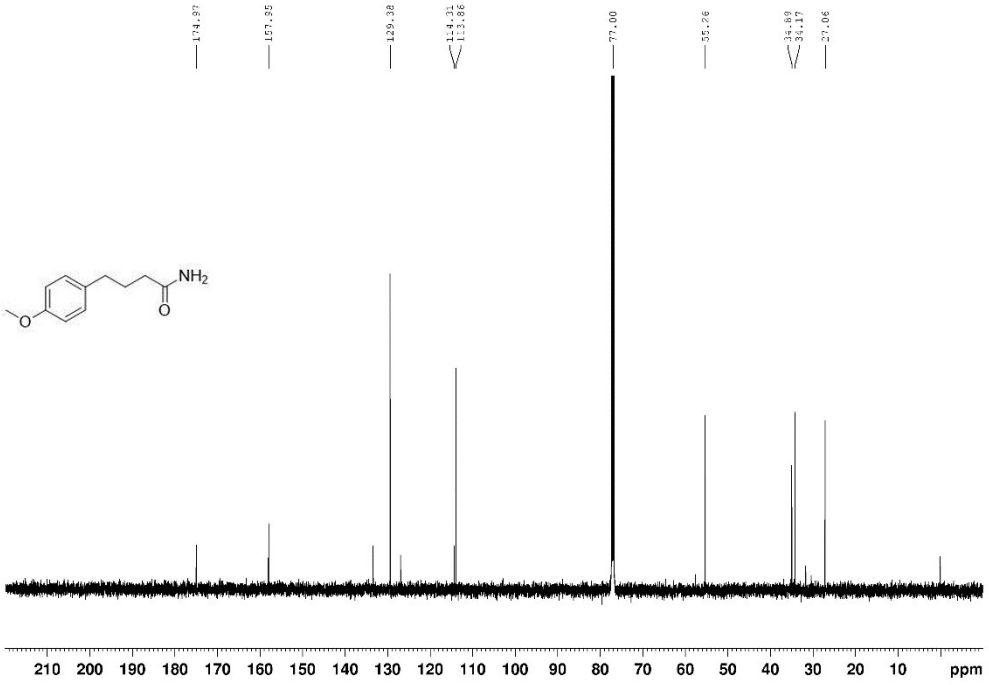
4ae, ^{19}F NMR, 376 M, DMSO-*d6*



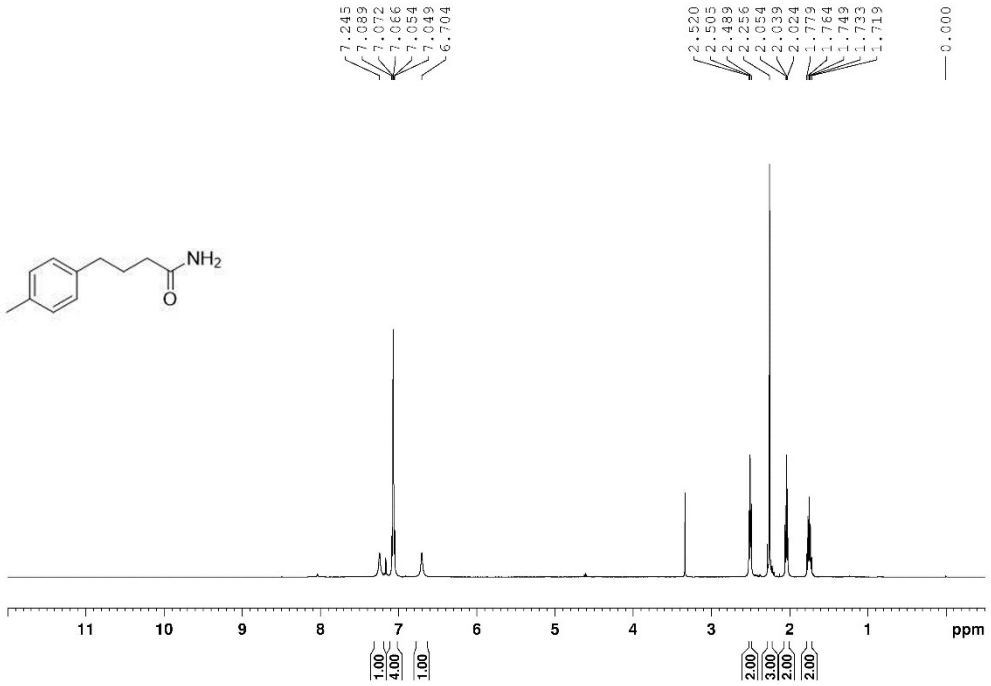
4af, ^{1}H NMR, 500 M, $CDCl_3$



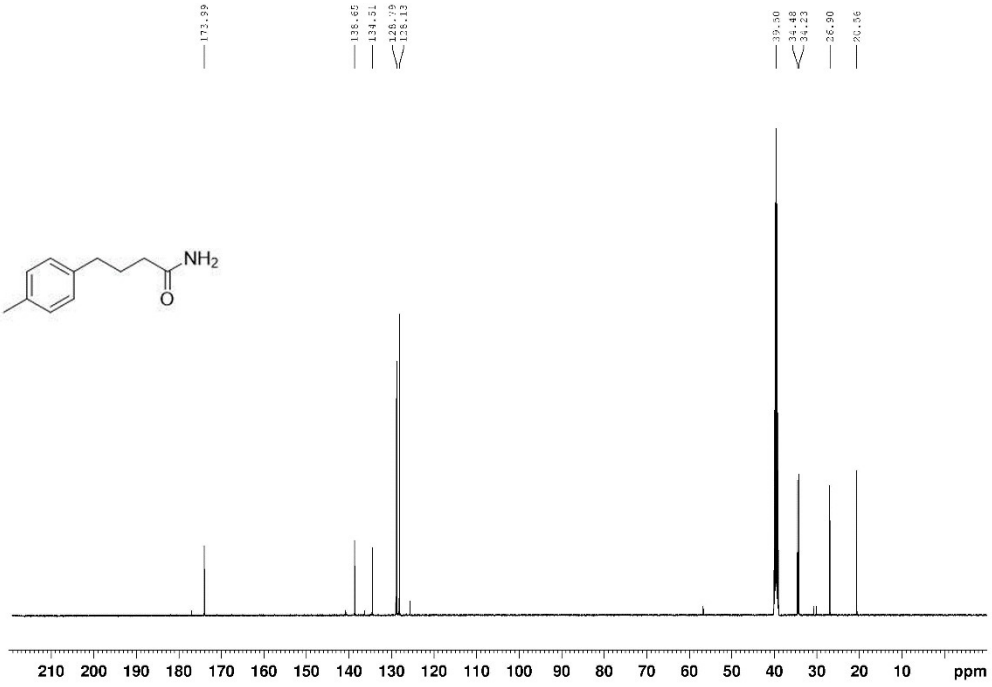
4af, ^{13}C NMR, 126 M, $CDCl_3$



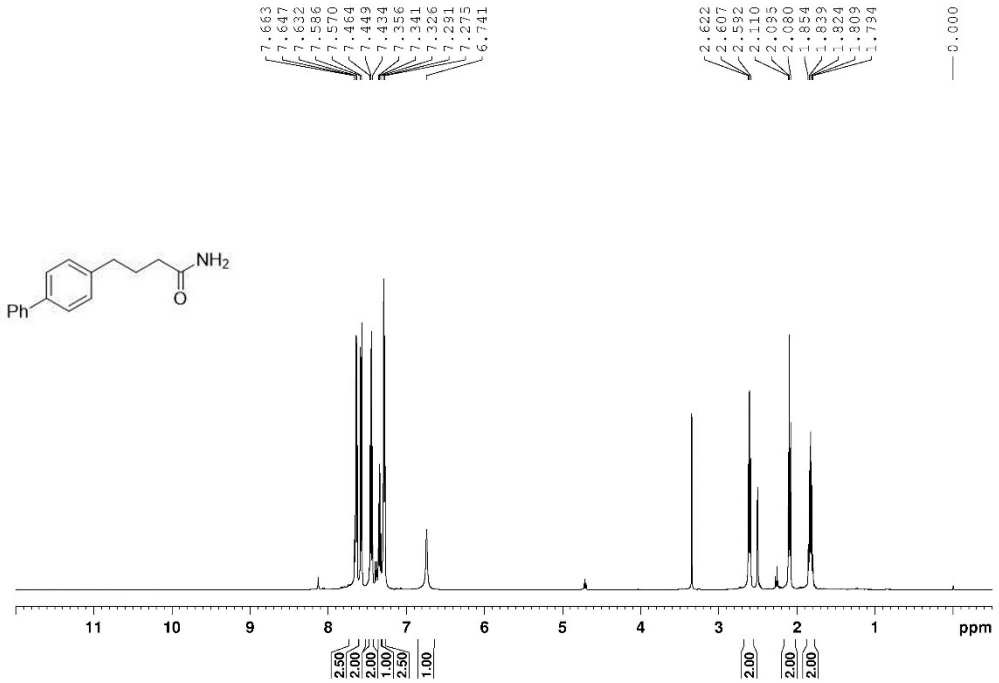
4ag, ^{1}H NMR, 500 M, DMSO-*d6*



4ag, ^{13}C NMR, 126 M, DMSO-*d6*



4ah, ^{1}H NMR, 500 M, DMSO-*d6*



4ah, ^{13}C NMR, 126 M, DMSO-*d6*