Urea Postmodified in Metal-Organic Framework as Catalytically Active Hydrogen-Bond Heterogeneous Catalyst

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Supporting Information

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Experimental Section

General Methods

NMR spectra were recorded on a Brüker DPX-300/400 spectrometer at 300/400 MHz for ^{1}H NMR and 75/100 MHz for ^{13}C NMR in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Mass spectra were determined on a Esquire-LC-00075 mass spectrometer. HRMS were recorded by using Agilent 6224 accurate-mass TOF LC/MS spectrometers. Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, TCI, and others).

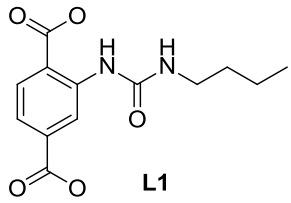
The synthesis of Cr-MIL-101-NH_2

Cr-MIL-101 was synthesized starting from $Cr(NO_3)_3 \cdot 9H_2O$ and terephthalic acid via hydrothermal reaction according to the literature.[S1] According to reported method,[S2] Cr-MIL-101–NO_2 was obtained by nitration of Cr-MIL-101 using a mixture solution of conc. HNO_3 and conc. H_2SO_4. Subsequently, the nitro groups were reduced to amino groups using anhydrous tin chloride. The physical properties of prepared MOFs match the literature.[S2]

Typical Experimental Procedures for the Synthesis of Cr-MIL-101-UR1~3:

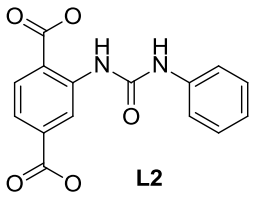
The Cr-MIL-101-NH_2 (200 mg) was soaked in CH_3CN (10 mL) and reacted with an appropriate isocynate (~5 eq.). After the sample was allowed to stand for 12 h at 120 °C in sealed tube, the resulting solid was isolated by filtration. The suspension of the obtained solid in acetone (50 mL) was heated at 60 ^{o}C for 1 h, and then filtered to collect the solid (repeating three times). Finally, the green solid was dried under vacuum at 40 ^{o}C for 12 hours to give title postmodified MOFs.

Cr-MIL-101-UR1:



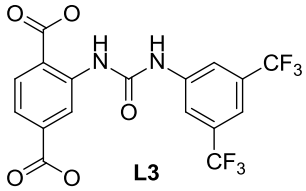
Elemental analysis calcd for $[Cr_3O(H_2O)_2F(L_1)_3]\bullet(H_2O)_5$ (%): C: 40.67, 4.90, 7.30; found: C: 41.07; H: 4.77; N: 7.21. IR (KBr pellet): ν 3327, 2960, 2870, 1618, 1551, 1427, 1387, 1302, 1269, 1157, 768, 661, 585 cm^{-1}. ^1H NMR (400 MHz, MeOD) δ 8.63 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 3.21 (t, *J* = 7.0 Hz, 2H), 1.60 – 1.48 (m, 2H), 1.45 – 1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ESI-MS: *m/z* $[M-H]^-$ 279.

Cr-MIL-101-UR2:



Elemental analysis calcd for $[Cr_3O(H_2O)_2F(L_2)_3]\bullet(H_2O)_5$ (%): C: 44.60; H: 3.66; N: 6.93; found: C: 45.02; H: 3.64; N: 6.65. IR (KBr pellet): ν 3314, 1690, 1597, 1544, 1427, 1387, 1312, 1267, 1267, 1224, 1037, 973, 907, 761, 693, 589 cm^{-1}. ^1H NMR (400 MHz, MeOD) δ 8.66 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.04 (t, *J* = 7.2 Hz, 1H). ESI-MS: *m/z* $[M-H]^-$ 299.

Cr-MIL-101-UR3:



Elemental analysis calcd for $[Cr_3O(H_2O)_2F(L_3)_3]\bullet(H_2O)_4$ (%): C 38.24, H 2.27, N 5.25; found: C: 38.46; H: 2.48; N: 5.06. IR (KBr pellet): ν 3394, 1698, 1623, 1566, 1428, 1388, 1281, 1182, 1136, 1046, 943, 888, 854, 806, 768, 677, 595, 532 cm^{-1}. ^1H NMR (400 MHz, MeOD) δ 8.74 (s, 1H), 8.06 (s, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.38 (s, 1H). ESI-MS: *m/z* $[M-H]^-$ 435.

Typical Experimental Procedures for the Characterization of Cr-MIL-101-UR1~3:

All elemental analyses were performed on a Flash EA 1112 elemental analyzer using 20 mg of the solid sample. ESI-MS analyses were performed on an Esquire-LC-00075 spectrometer using the digested solution of 0.5 mg of the sample in 0.24 mL of methanol and 0.1 mL of sodium hydroxide (40 wt% aqueous solution) and followed by acidification. ^1H NMR analyses were performed on Brüker DPX-400

spectrometer using the digested solution of 10 mg of the sample in 0.48 mL of methanol-d_4 and 0.2 mL of sodium deuteroxide (40 wt% solution in D_2O). All infrared experiments were performed on a Brüker Alpha FT-IR spectrometer using 1mg of the solid sample at 20 ^oC at a 4 cm^{-1} resolution.

PXRD Analysis

Powder X-ray diffraction (PXRD) data were collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Kα (λ= 1.5418 Å), with a scan speed of 3 sec/step, a step size of 0.02° and a 2θ range of 5-45º. The experimental background was corrected using the Brüker EVA 2 software.

Emission scanning electron microscope (SEM) analysis

A Hitachi S-4800 field emission scanning electron microscope (SEM) was used to determine particle size and morphology. Each SEM sample was prepared by suspending the sample in ethanol. A drop of the suspension was then placed on a glass slide and the solvent was allowed to evaporate.

Thermogravimetric Analysis

Approximately 20 mg of modified MIL-101 samples was used for thermogravimetric analysis (TGA) measurements using a Perkin Elmer TGA 7 running from 30 ^oC to 600 ^oC with a scan rate of 3 ^oC/min.

Brunauer−Emmer−Teller (BET) Surface Areas Analysis

The Brunauer−Emmer−Teller (BET) surface areas and porosity were measured by Micromeritics ASAP 2020 analyzer at 77 K. Each time, approximately 60 mg sample was evacuated in a vacuum oven at 70 ^oC overnight. The sample was then transferred to preweighed quarz tube and degassed at 70 ^oC until the system pressure < 5 μmHg. Afterwards, the tube was reweighed to obtain an accurate mass for BET surface area determination.

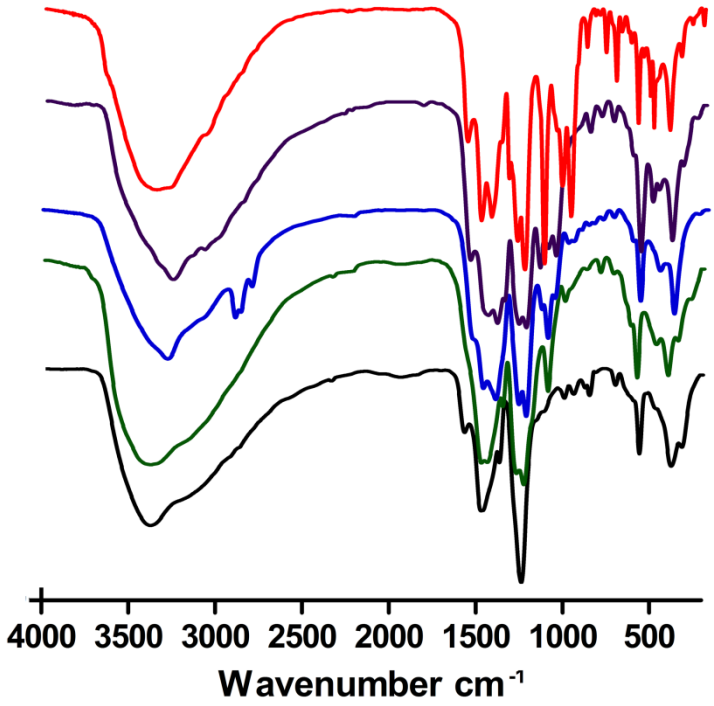


Fig. S1. IR spectra of Cr-MIL-101 (black), Cr-MIL-101–NH_2 (green), Cr-MIL-101-UR**1** (blue), Cr-MIL-101-UR**2** (purple) and Cr-MIL-101-UR**3** (red).

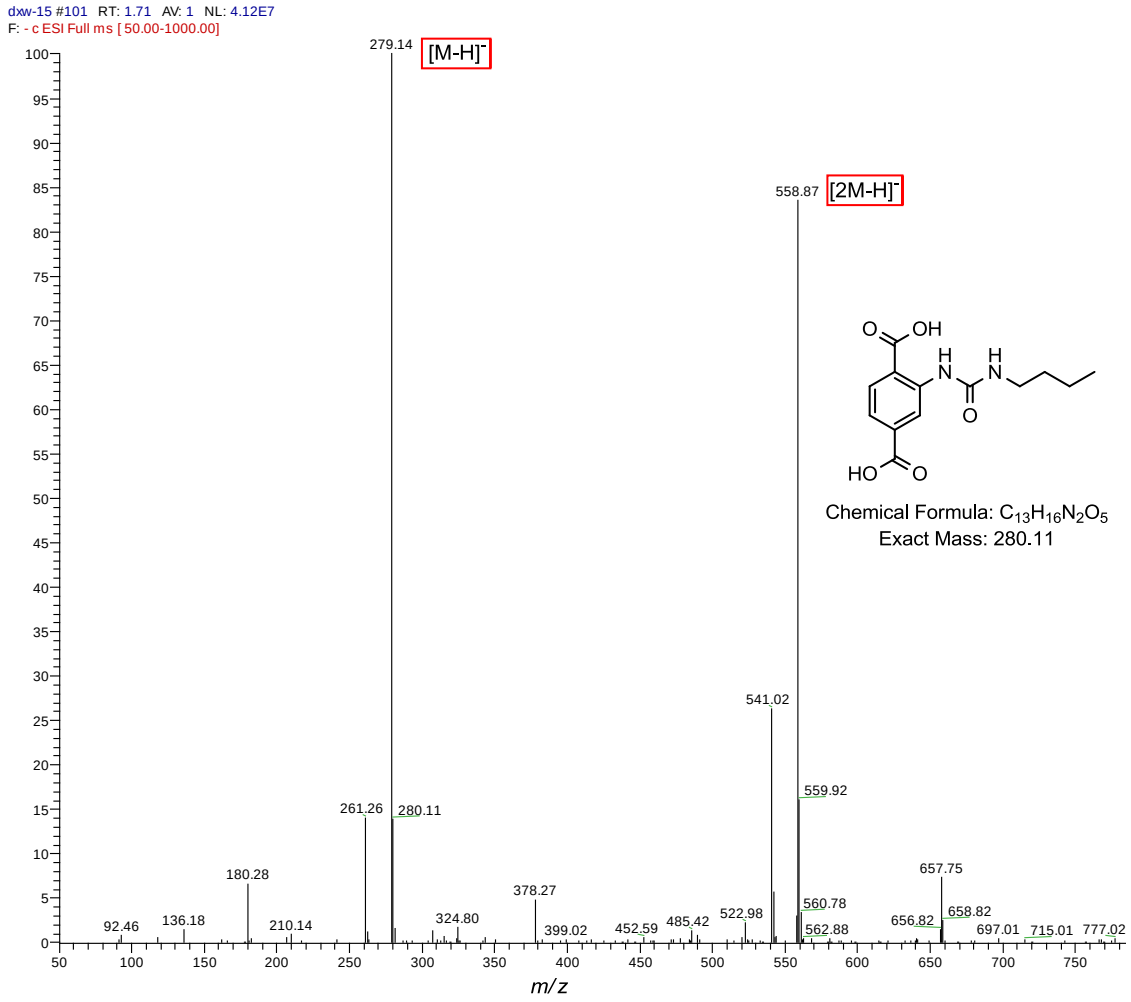


Fig. S2a. ESI-MS (negative mode) of Cr-MIL-101-UR**1**.

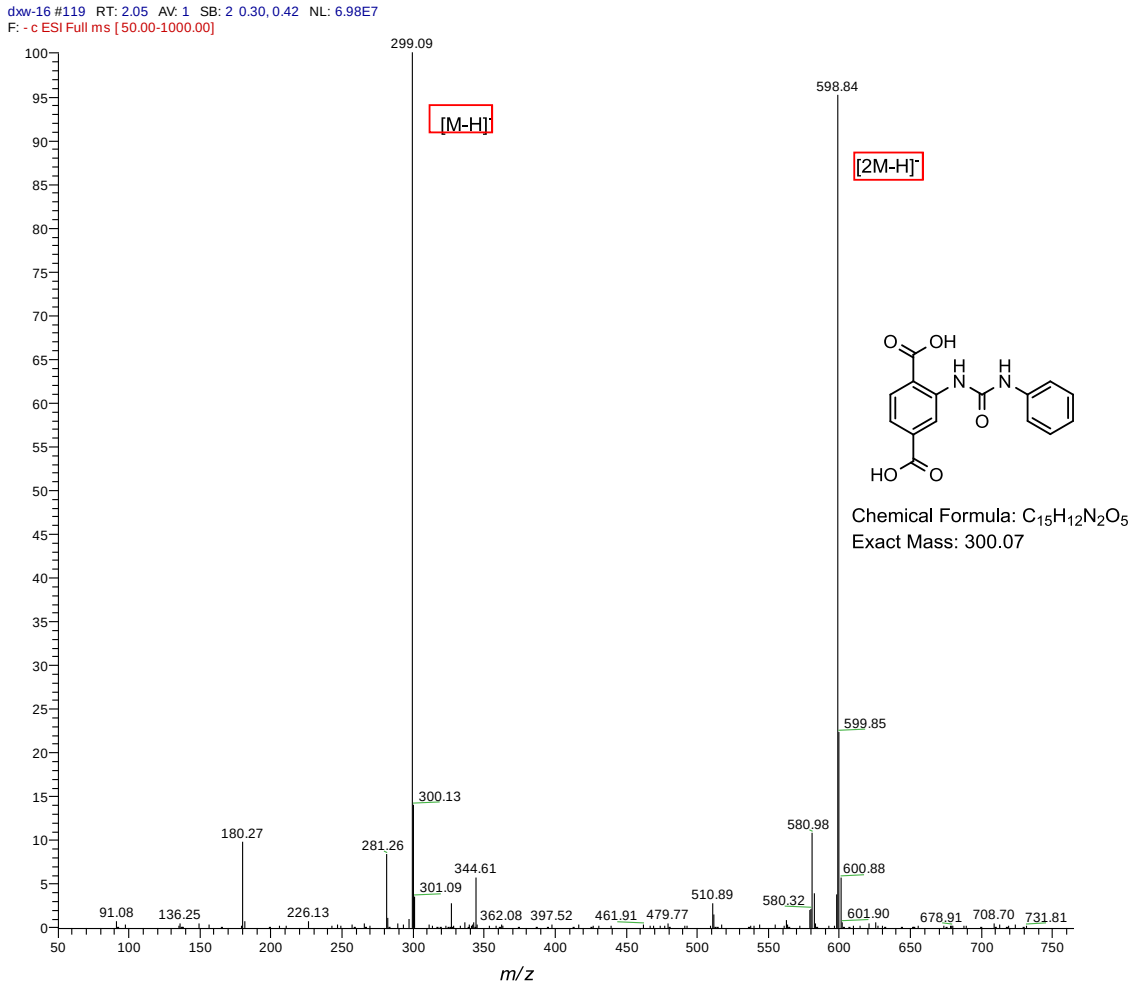


Fig. S2b. ESI-MS (negative mode) of Cr-MIL-101-UR**2**.

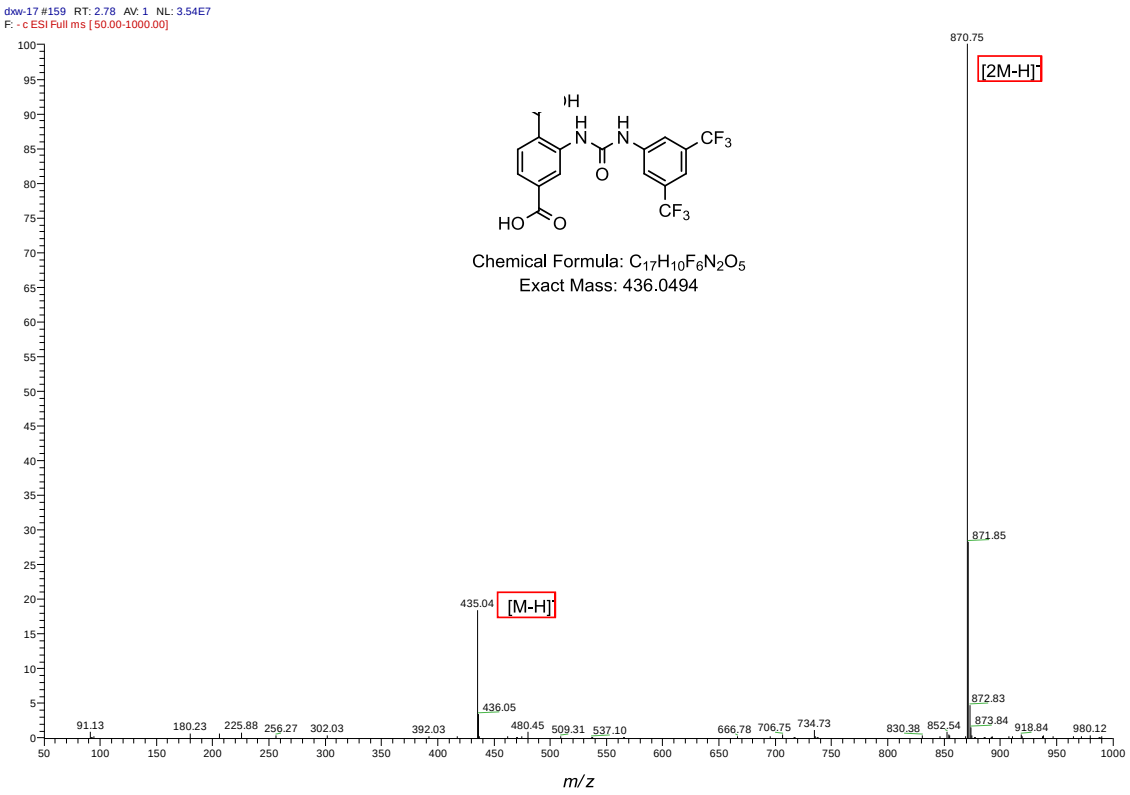


Fig. S2c. ESI-MS (negative mode) of Cr-MIL-101-UR**3**.

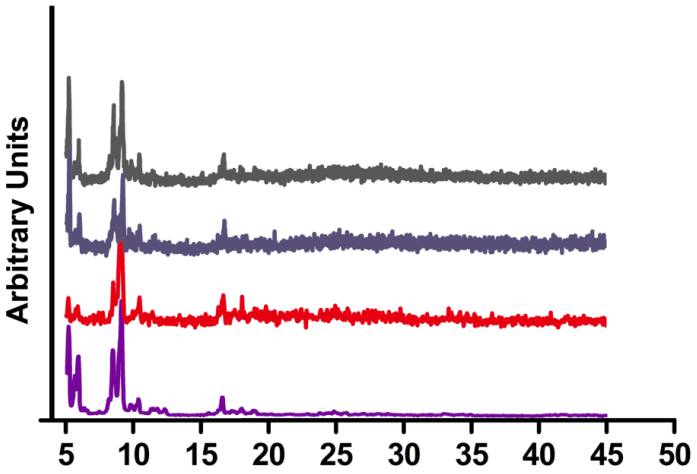


Fig. S3. PXRD measurements of Cr-MIL-101–UR**1** (black), Cr-MIL-101–UR**2** (blue), Cr-MIL-101–UR**3** (red) and Cr-MIL-101 (purple).

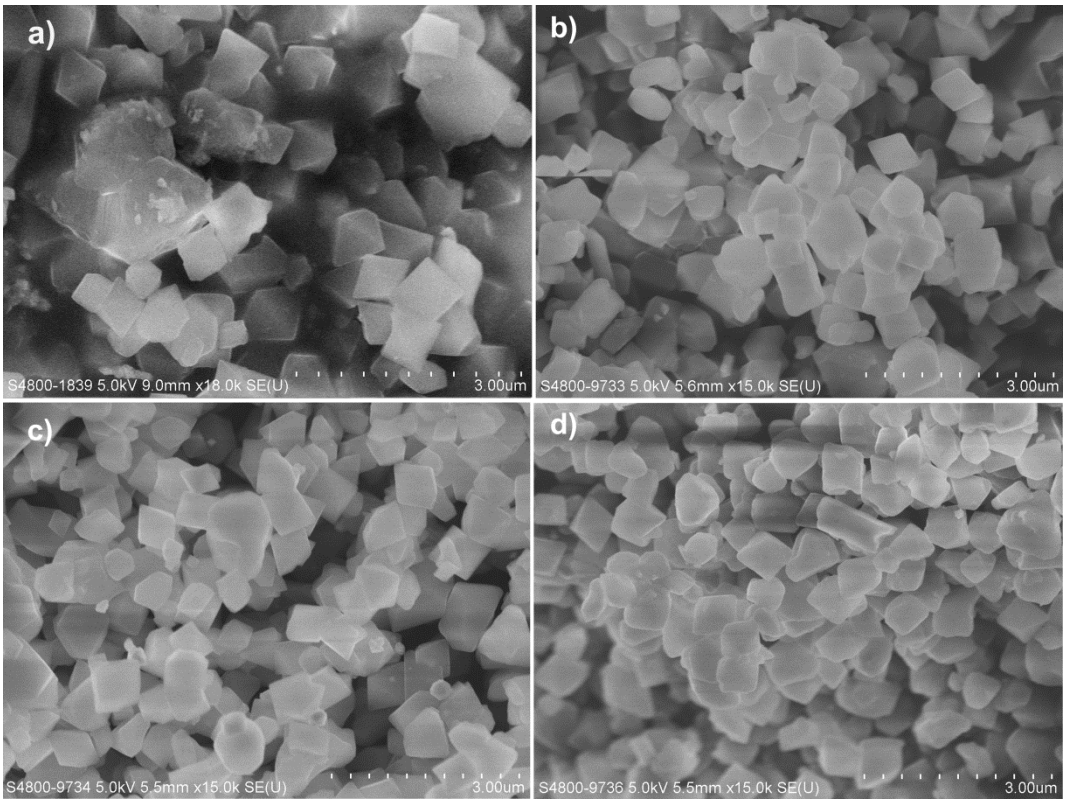


Fig. S4. SEM image of (a) Cr-MIL-101, (b) Cr-MIL-101-UR**1**, (c) Cr-MIL-101-UR**2** and (d) Cr-MIL-101-UR**3**.

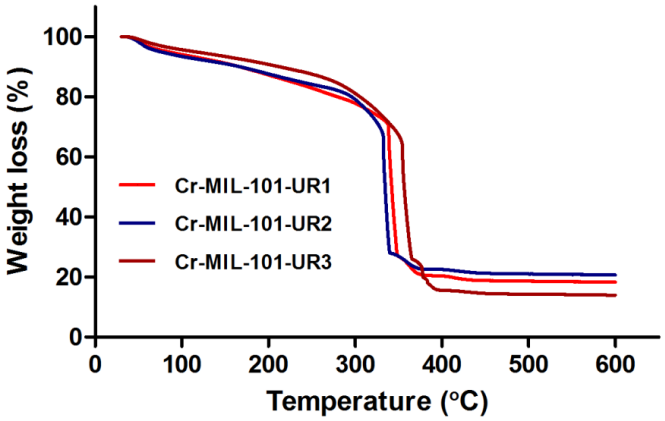


Fig. S5. Thermogravimetric analyses of Cr-MIL-101-UR**1** (Red)**,** Cr-MIL-101-UR**2** (Blue) and Cr-MIL-101-UR**3** (Brown).

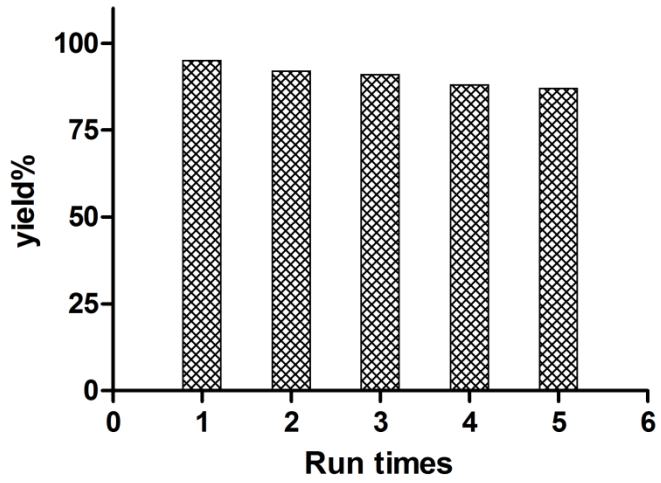


Fig. S6. The recyclable results of Cr-MIL-101-UR**3**-catalyzed Friedel-Crafts alkylation of **1A** (0.5 mmol) with **2d** (0.6 mmol) in the presence of Cr-MIL-101-UR**3** (0.075 mmol) at 60 ^{o}C for 30 h and yield was determined by ^{1}H NMR spectrum.

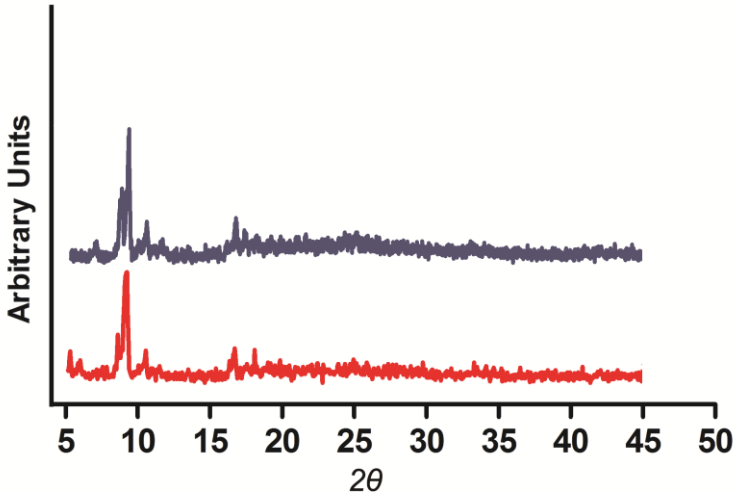
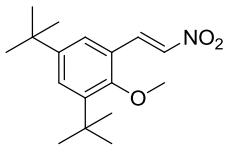


Fig. S7. PXRD measurements of unreacted Cr-MIL-101–UR**3** (red), and recyclable Cr-MIL-101–UR**3** (black).

Typical Experimental Procedures for the Syntheses of nitrovinyl substrates 1B-H and 1J-K

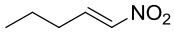
Different aldehydes (1 mmol) and nitromethane (3 mL) was introduced into a flask; a catalytic amount of ammonium acetate (0.3 mmol) was added and then refluxed for 5 hours. The reaction mixture was cooled and treated with ethyl acetate (10 mL) and water (20 mL) and then extracted by ethyl acetate (20 mL × 3). The combined extraction was washed by brine, dried over anhydrous $NaSO_4$ and concentrated in vacuum. The residue was purified by silica-gel column chromatography using *n*-hexane: ethyl acetate as eluant to give title compounds. **1B-C**[S3], **1D**[S4], **1E-F**[S3], **1H**[S5], and **1J**[S7] were prepared and the physical properties match those reported in the literature.

(*E*)-1,5-di-tert-butyl-2-methoxy-3-(2-nitrovinyl)benzene (1K)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 13.7 Hz, 1H), 7.66 (d, *J* = 13.7 Hz, 1H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.32 (d, *J* = 2.3 Hz, 1H), 3.79 (s, 3H), 1.41 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 146.6, 143.2, 137.3, 136.3, 128.8, 124.0, 123.5, 63.8, 35.4, 34.6, 31.3, 30.8. ESI-MS: *m/z* $[M+H]^+$ 292. HR-MS (ESI): Calcd. for $[M+H]^+$: 292.1913, found: 292.1918.

(*E*)-1-nitropent-1-ene (1I)[S6]

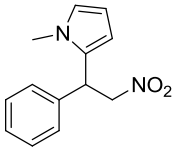


To a mixture of butyraldehyde (3.27 g, 45.3 mmol) and nitromethane (2.77 g, 45.3 mmol) in methanol (10 mL) was added a solution of NaOH in H_2O (2.18 g, 54.4 mmol in 2 mL) dropwise at 0 °C. Further methanol (2 mL) was added and the resulting yellow slurry was stirred at that temperature for 1 h. Water (30 mL) was added and the clear yellow solution was poured into 3N hydrochloric acid and stirred for 15 min. The aqueous mixture was extracted with DCM (20 mL x 3), the combined organic layers were dried over anhydrous $NaSO_4$ and concentrated in vacuum. The residue was purified by column chromatography using n-hexane: ethyl acetate as eluant (20/1, v/v) to obtain a yellow liquid. The physical properties match those reported in the literature[S6].

Typical Experimental Procedure for Cr-MIL-101-UR3-catalyzed Friedel-Crafts Reaction

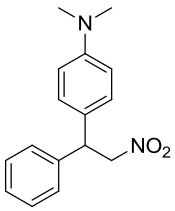
A solution of nitro vinyl substrate (0.1 mmol) and electron-rich nucleophiles (0.12 mmol) in CH_3CN (0.15 mL) was added Cr-MIL-101-UR**3** (0.015 mmol). The suspension was heated at 60 ^oC for 18~36 hours. The reaction mixture was then cooled and filtered. The filtration was concentrated in vacuum and then purified by silica-gel column chromatography using *n*-hexane: ethyl acetate as eluant to give title products.

1-Methyl-2-(2-nitro-1-phenylethyl)-1H-pyrrole (3Aa)[S8]



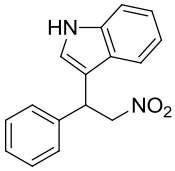
^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 4H), 7.20 – 7.10 (m, 2H), 6.62 – 6.54 (m, 1H), 6.18 – 6.06 (m, 2H), 4.94 (dd, *J* = 12.0, 7.9 Hz, 1H), 4.90 – 4.82 (m, 1H), 4.74 (dd, *J* = 12.0, 7.3 Hz, 1H), 3.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 129.2, 128.9, 128.0, 128.0, 123.1, 107.0, 106.0, 79.6, 41.9, 33.9. ESI-MS: *m/z* $[M+H]^+$ 231.

***N,N*-dimethyl-4-(2-nitro-1-phenylethyl)aniline (3Ab)[S9]**



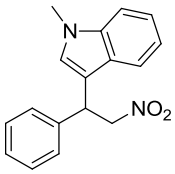
^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 2H), 7.26 – 7.17 (m, 3H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 8.6 Hz, 2H), 5.07 – 4.85 (m, 2H), 4.80 (t, *J* = 8.1 Hz, 1H), 2.91 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 140.1, 129.0, 128.4, 127.7, 127.4, 126.7, 112.8, 79.72, 48.3, 40.5. ESI-MS: *m/z* $[M+H]^+$ 271.

3-(2-nitro-1-phenylethyl)-1H-indole (3Ac)[S8]



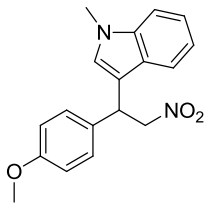
^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.40 – 7.24 (m, 6H), 7.24 – 7.13 (m, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 1.7 Hz, 1H), 5.19 (t, *J* = 7.8 Hz, 1H), 5.06 (dd, *J* = 12.5, 7.6 Hz, 1H), 4.94 (dd, *J* = 12.5, 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 136.6, 129.0, 127.9, 127.7, 126.2, 122.8, 121.7, 120.0, 119.0, 114.5, 111.5, 79.6, 41.6. ESI-MS: *m/z* $[M+H]^+$ 267.

1-methyl-3-(2-nitro-1-phenylethyl)-1H-indole (3Ad)[S8]



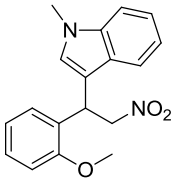
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.18 (m, 7H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.85 (s, 1H), 5.18 (t, *J* = 8.0 Hz, 1H), 5.04 (dd, *J* = 12.5, 7.5 Hz, 1H), 4.93 (dd, *J* = 12.5, 8.5 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 137.4, 129.0, 127.8, 127.6, 126.6, 126.5, 122.3, 119.6, 119.1, 112.9, 109.6, 79.6, 41.6, 32.9. ESI-MS: *m/z* $[M+H]^+$ 281.

3-(1-(4-methoxyphenyl)-2-nitroethyl)-1-methyl-1H-indole (3Bd)[S10]



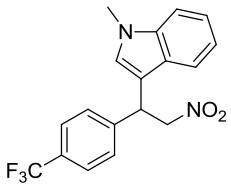
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.13 (m, 5H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 7.4 Hz, 3H), 5.12 (t, *J* = 7.9 Hz, 1H), 5.01 (dd, *J* = 12.2, 7.5 Hz, 1H), 4.87 (dd, *J* = 12.1, 8.7 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 137.4, 131.4, 128.9, 126.6, 126.3, 122.3, 119.5, 119.1, 114.3, 113.2, 109.6, 79.9, 55.3, 40.9, 32.9. ESI-MS: *m/z* $[M+H]^+$ 311.

3-(1-(2-methoxyphenyl)-2-nitroethyl)-1-methyl-1H-indole (3Cd)



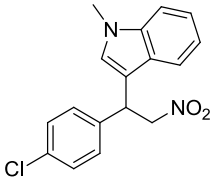
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.18 (m, 4H), 7.13 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.97 (s, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 5.70 – 5.50 (m, 1H), 5.01 (qd, *J* = 12.5, 7.9 Hz, 2H), 3.92 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 137.3, 129.0, 128.7, 127.5, 127.1, 126.8, 122.1, 120.9, 119.3, 119.3, 112.4, 110.9, 110.1, 109.5, 78.3, 55.6, 35.5, 32.9. ESI-MS: *m/z* $[M+H]^+$ 311. HR-MS(ESI): Calcd. for $[M+H]^+$: 311.1396, found: 311.1402.

1-methyl-3-(2-nitro-1-(4-(trifluoromethyl)phenyl)ethyl)-1H-indole (3Dd)[S11]



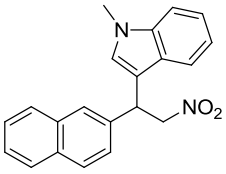
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.28 – 7.16 (m, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.85 (s, 1H), 5.24 (t, *J* = 7.9 Hz, 1H), 5.06 (dd, *J* = 12.7, 7.2 Hz, 1H), 4.95 (dd, *J* = 12.7, 8.8 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 137.4, 128.3, 126.5, 126.4, 126.1, 126.0, 126.0, 126.0, 122.6, 119.8, 118.8, 109.8, 79.1, 41.4, 33.0. ESI-MS: *m/z* $[M+H]^+$ 349.

3-(1-(4-chlorophenyl)-2-nitroethyl)-1-methyl-1H-indole (3Ed)[S12]



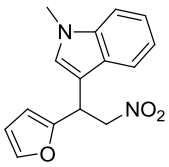
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.22 (dd, *J* = 13.2, 6.4 Hz, 4H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.83 (s, 1H), 5.13 (t, *J* = 7.9 Hz, 1H), 5.02 (dd, *J* = 12.5, 7.3 Hz, 1H), 4.88 (dd, *J* = 12.5, 8.7 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.2, 132.8, 129.4, 128.7, 126.2, 122.3, 119.5, 118.8, 114.2, 112.1, 109.5, 79.1, 40.9, 32.8. ESI-MS: *m/z* $[M+H]^+$ 315, 317.

1-methyl-3-(1-(naphthalen-2-yl)-2-nitroethyl)-1H-indole (3Fd)



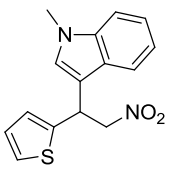
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 4H), 7.53 – 7.36 (m, 4H), 7.23 (dt, *J* = 12.4, 8.1 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.86 (s, 1H), 5.34 (t, *J* = 8.0 Hz, 1H), 5.07 (qd, *J* = 12.6, 8.0 Hz, 2H), 3.71 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 136.9, 133.5, 132.8, 128.8, 128.0, 127.7, 126.6, 126.4, 126.4, 126.1, 125.9, 122.3, 119.6, 119.1, 112.8, 109.6, 79.5, 41.7, 32.9. ESI-MS: *m/z* $[M+H]^+$ 331. HR-MS (ESI): Calcd. for $[M+H]^+$: 311.1447, found: 311.1452.

3-(1-(furan-2-yl)-2-nitroethyl)-1-methyl-1H-indole (3Gd)[S10]



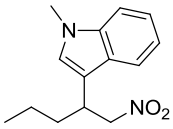
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 1.1 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.22 (m, 1 H), 7.23 – 7.08 (m, 1H), 6.99 (s, 1H), 6.32 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.18 (d, *J* = 3.2 Hz, 1H), 5.25 (t, *J* = 7.8 Hz, 1H), 5.05 (dd, *J* = 12.5, 8.2 Hz, 1H), 4.91 (dd, *J* = 12.5, 7.3 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 142.3, 137.2, 127.4, 126.2, 122.3, 119.7, 118.9, 110.5, 110.0, 109.7, 107.4, 78.1, 35.7, 32.9. ESI-MS: *m/z* $[M+H]^+$ 271.

1-methyl-3-(2-nitro-1-(thiophen-2-yl)ethyl)-1H-indole (3Hd)[S10]



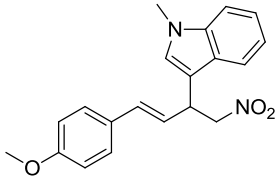
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.21 (d, *J* = 5.0 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.03 – 6.93 (m, 3H), 5.47 (t, *J* = 7.9 Hz, 1H), 5.08 – 4.94 (m, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 137.3, 127.0, 126.7, 126.3, 125.2, 124.9, 122.4, 119.7, 119.0, 112.5, 109.7, 80.2, 37.0, 33.0. ESI-MS: *m/z* $[M+H]^+$ 287.

1-methyl-3-(1-nitropentan-2-yl)-1H-indole (3Id)



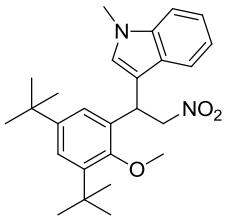
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.89 (s, 1H), 4.74 – 4.54 (m, 2H), 3.84 – 3.75 (m, 1H), 3.75 (s, 3H), 1.98 – 1.62 (m, 2H), 1.40 – 1.20 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.3, 126.8, 126.7, 122.0, 119.3, 118.9, 112.6, 109.7, 80.8, 36.1, 34.8, 32.9, 20.5, 14.0. ESI-MS: *m/z* $[M+H]^+$ 247. HR-MS (ESI): Calcd. for $[M+H]^+$: 247.1447, found: 247.1455.

(*E*)-3-(1-(4-methoxyphenyl)-4-nitrobut-3-en-1-yl)-1-methyl-1H-indole (3Jd)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.21 (m, 5H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.95 (s, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.27 (dd, *J* = 15.8, 7.6 Hz, 1H), 4.83 (dd, *J* = 11.8, 6.7 Hz, 1H), 4.75 (dd, *J* = 11.8, 8.6 Hz, 1H), 4.66 (dd, *J* = 15.2, 7.6 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 137.4, 132.0, 129.4, 127.8, 126.5, 124.9, 122.3, 119.6, 119.1, 114.1, 111.8, 109.8, 79.7, 55.4, 39.6, 32.9. ESI-MS: *m/z* $[M+H]^+$ 337. HR-MS (ESI): Calcd. for $[M+H]^+$: 337.1552, found: 337.1559.

3-(1-(3,5-di-tert-butyl-2-methoxyphenyl)-2-nitroethyl)-1-methyl-1H-indole (3Kd)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.33 – 7.21 (m, 4H), 7.18 (d, *J* = 2.3 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.82 (s, 1H), 5.61 (t, *J* = 8.0 Hz, 1H), 5.01 (dd, *J* = 12.6, 7.9 Hz, 1H), 4.92 (dd, *J* = 12.5, 8.1 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 1.40 (s, 9H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 145.9, 142.7, 137.5, 131.8, 127.3, 126.9, 123.6, 123.3, 122.3, 119.6, 119.1, 113.3, 109.6, 79.5, 62.7, 35.6, 35.1, 34.7, 33.0, 31.6, 31.3. ESI-MS: *m/z* $[M+H]^+$ 423. HR-MS (ESI): Calcd. for $[M+H]^+$: 423.2648, found: 423.2656.

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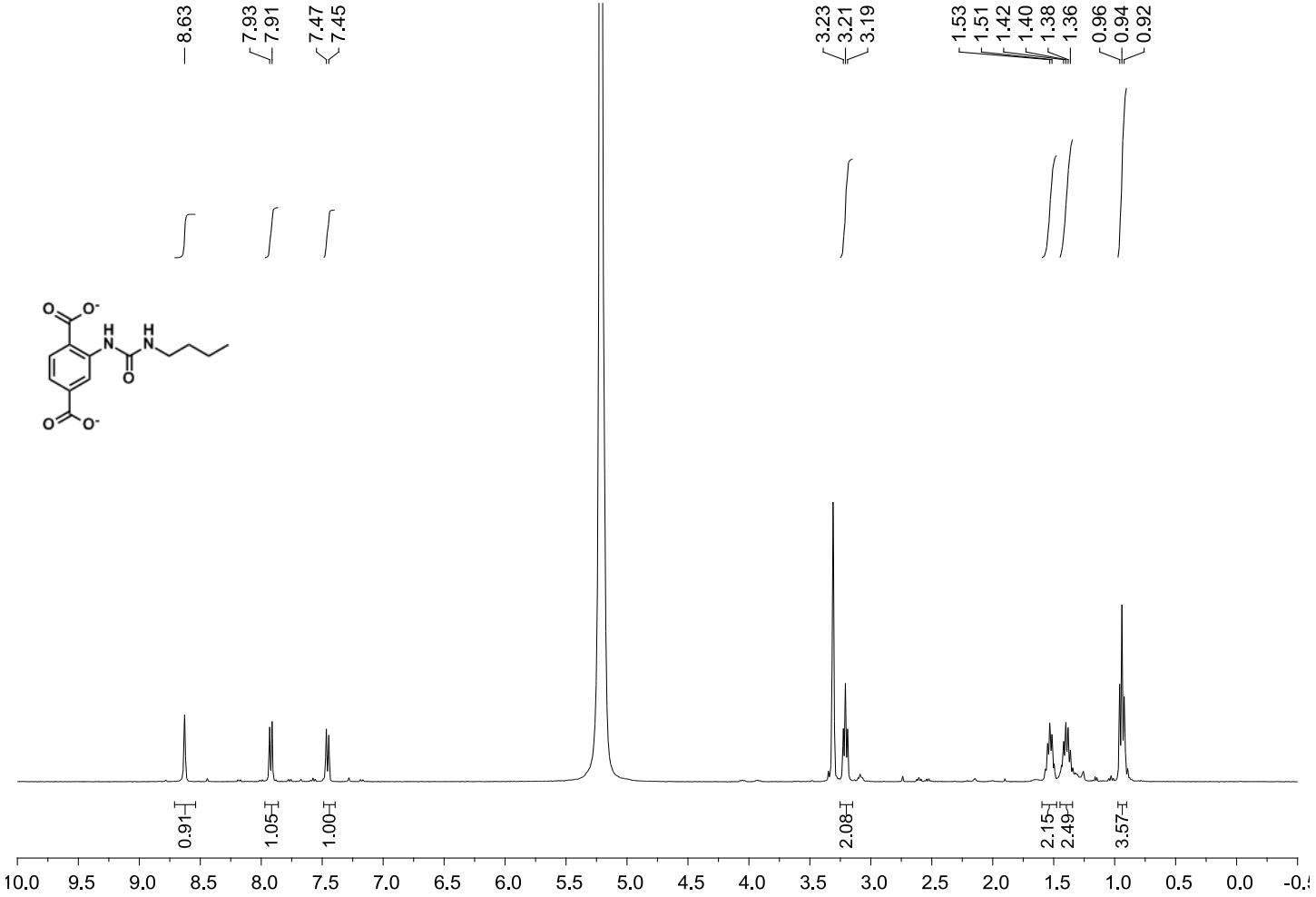
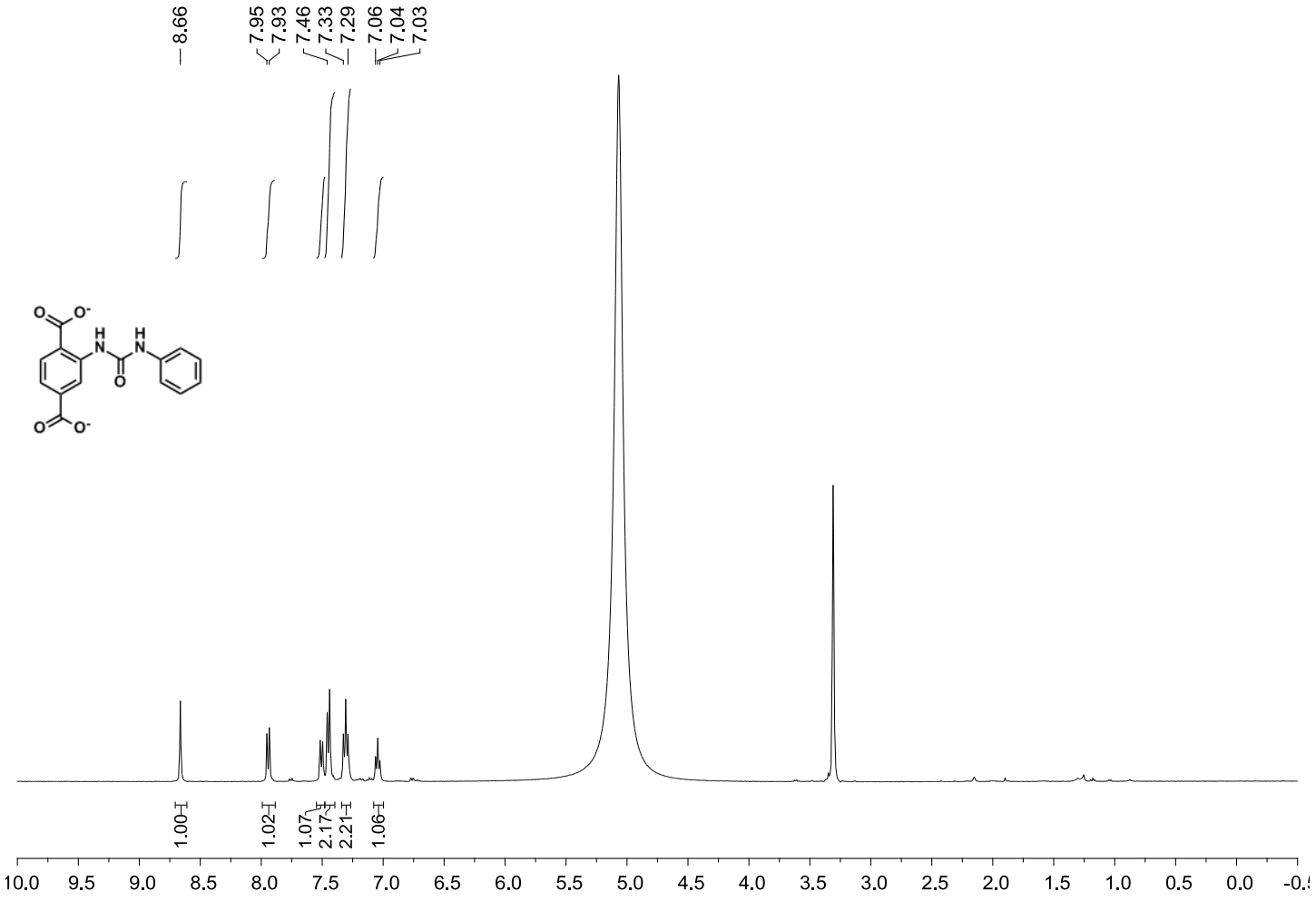
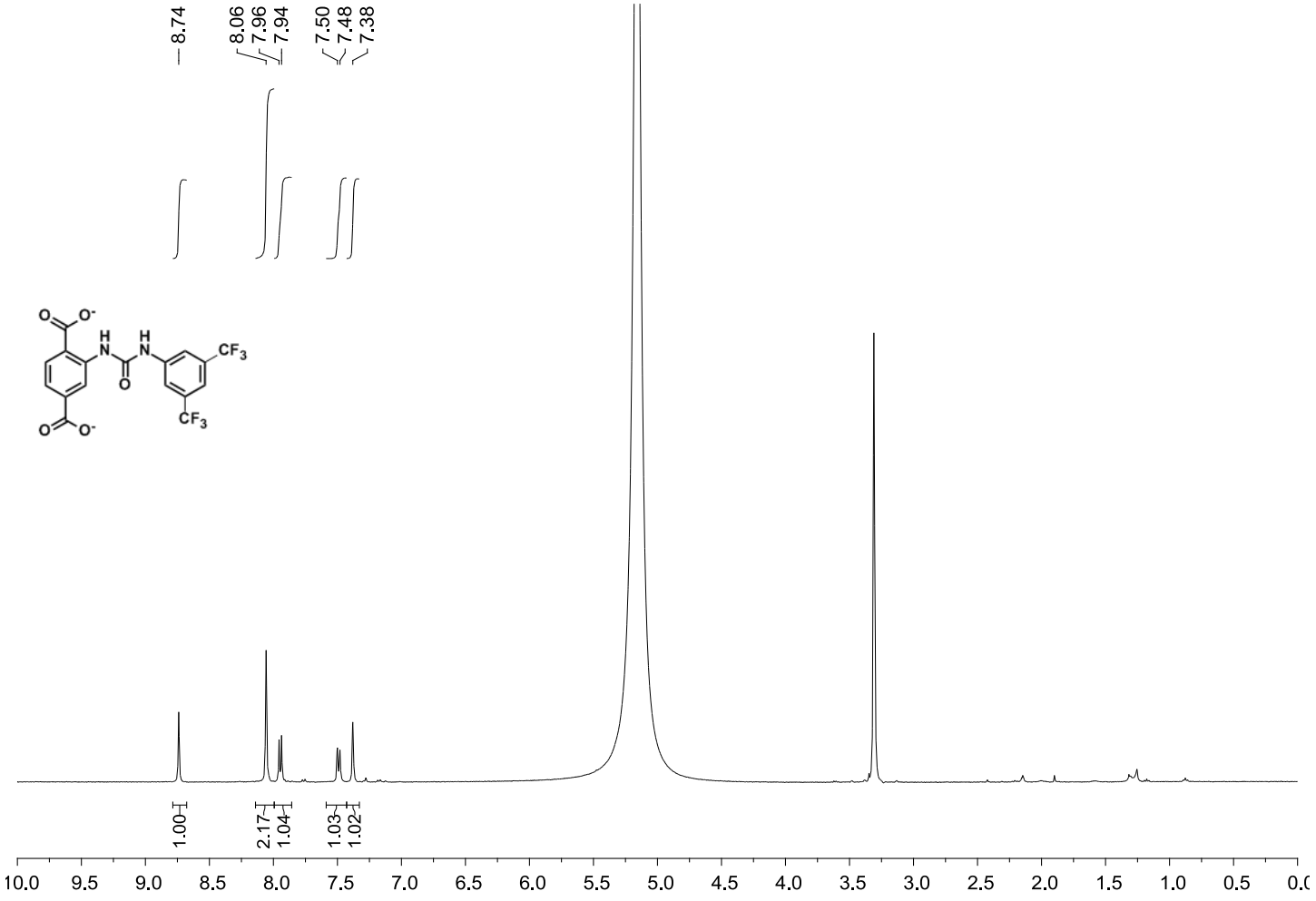
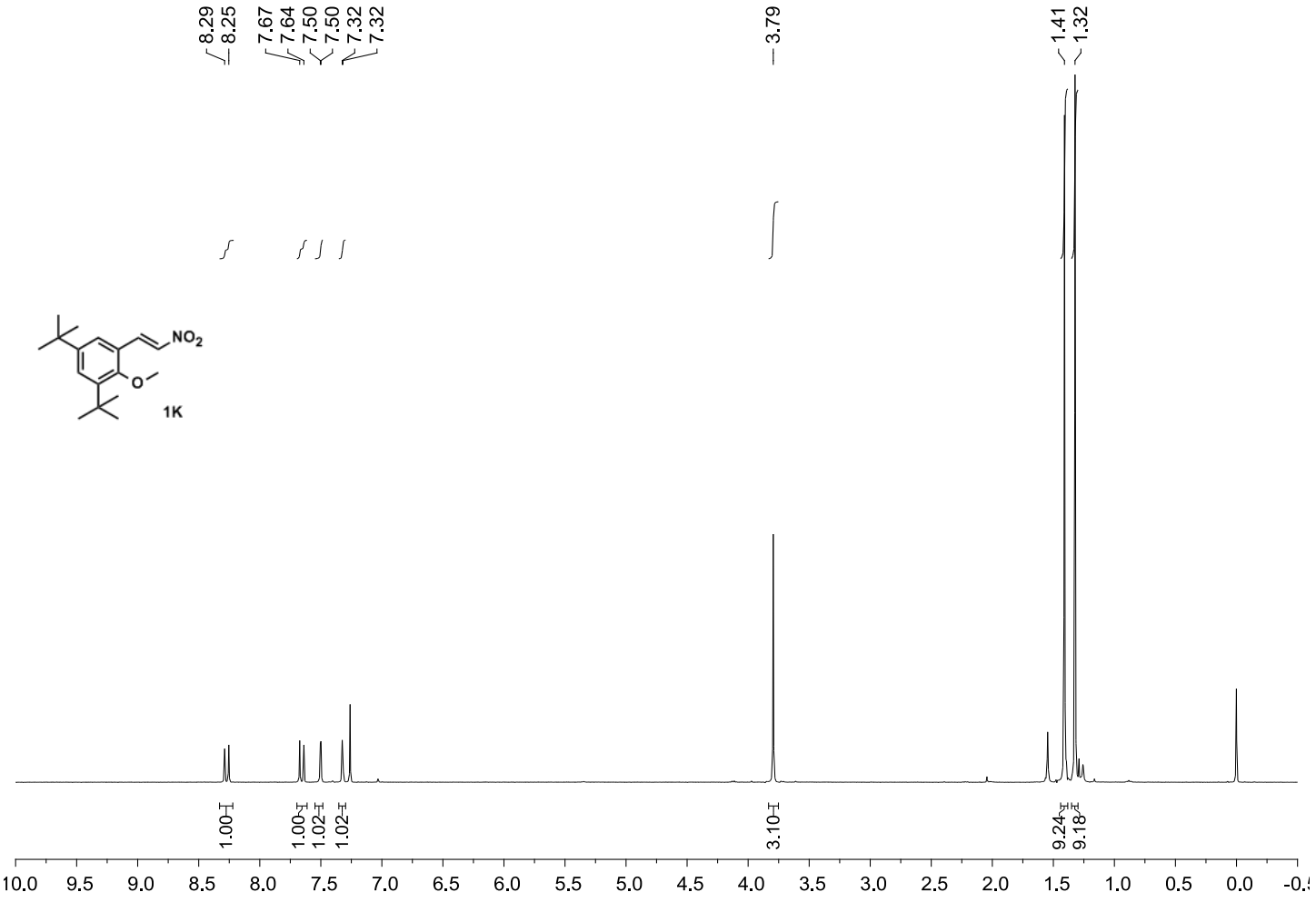
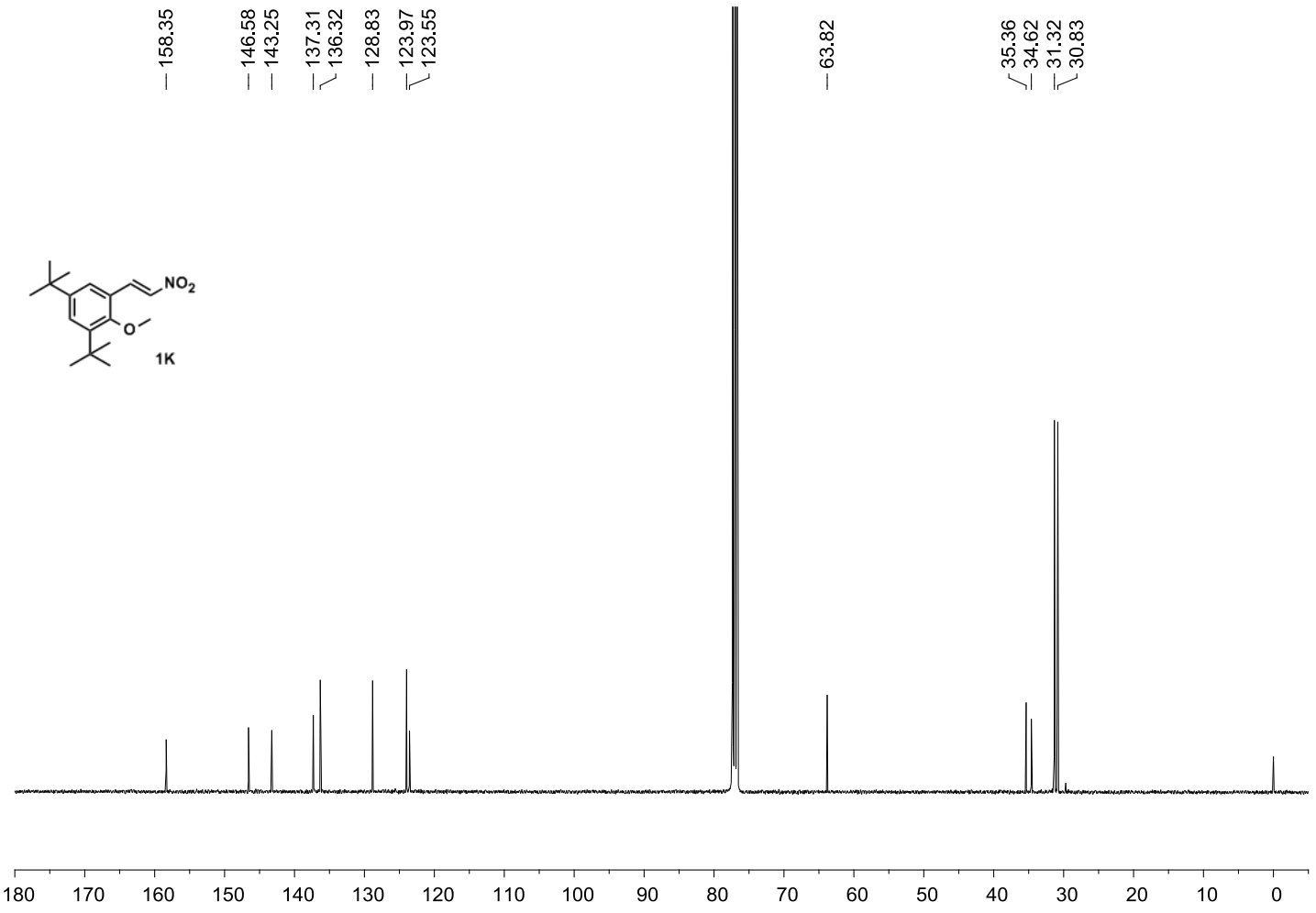
Spectra:

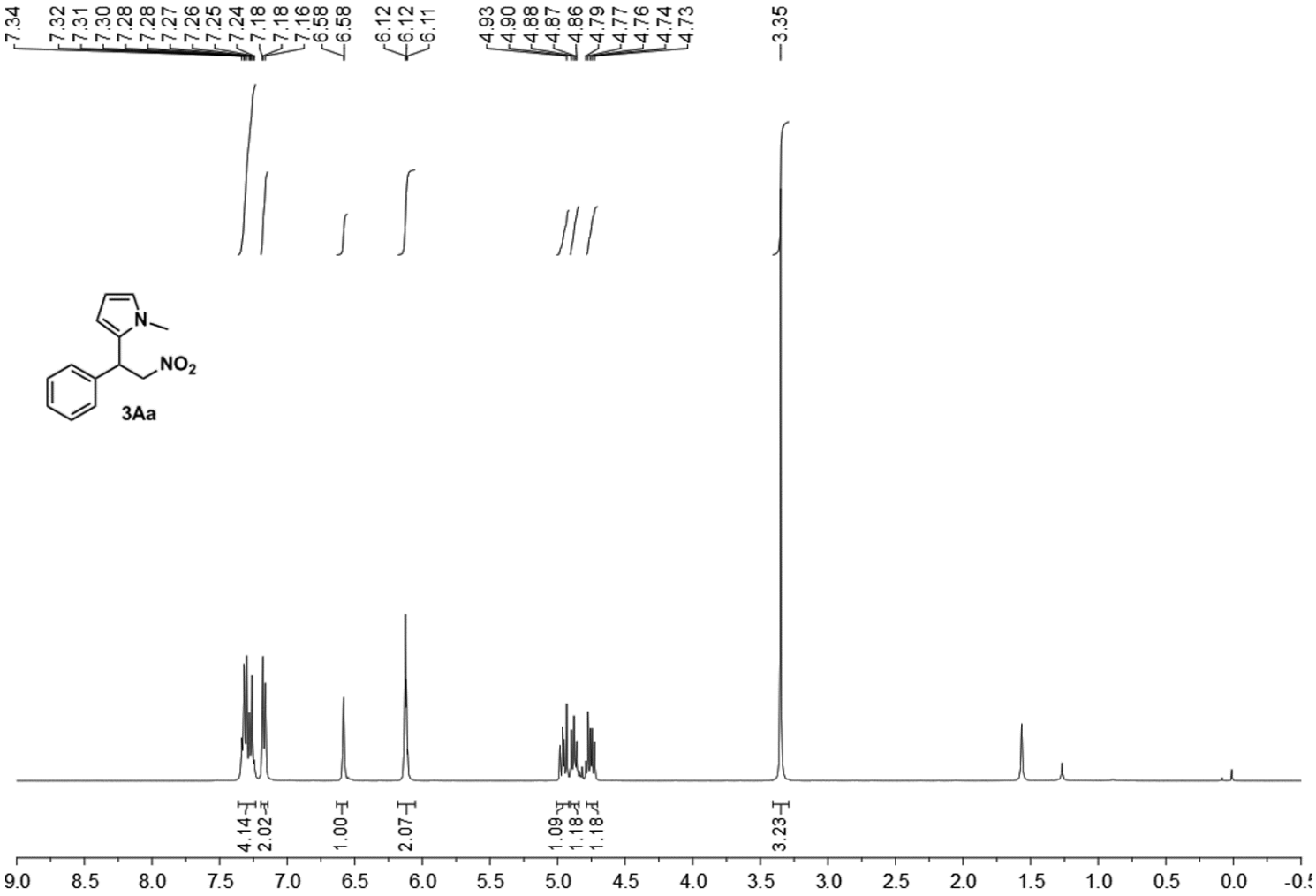


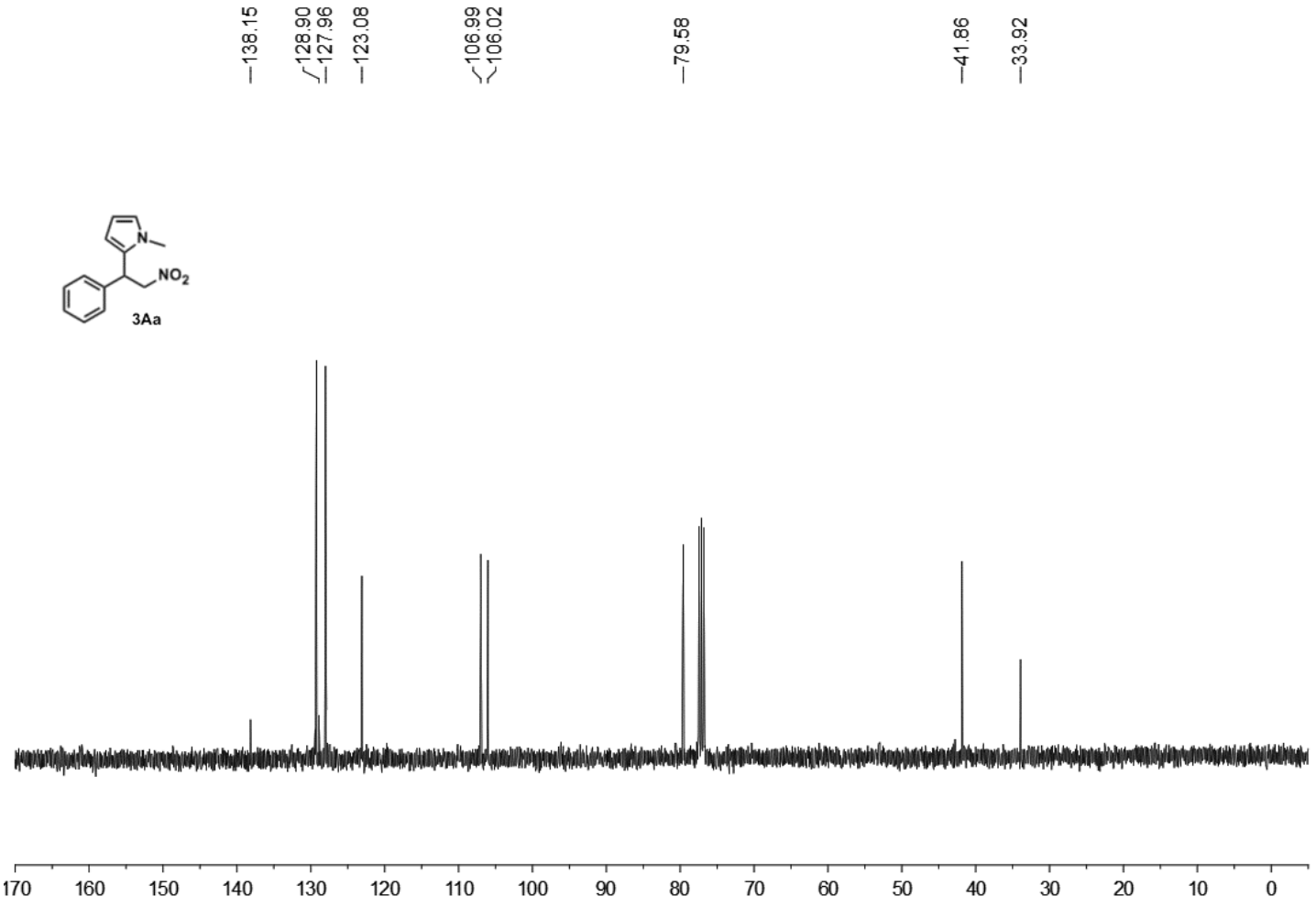


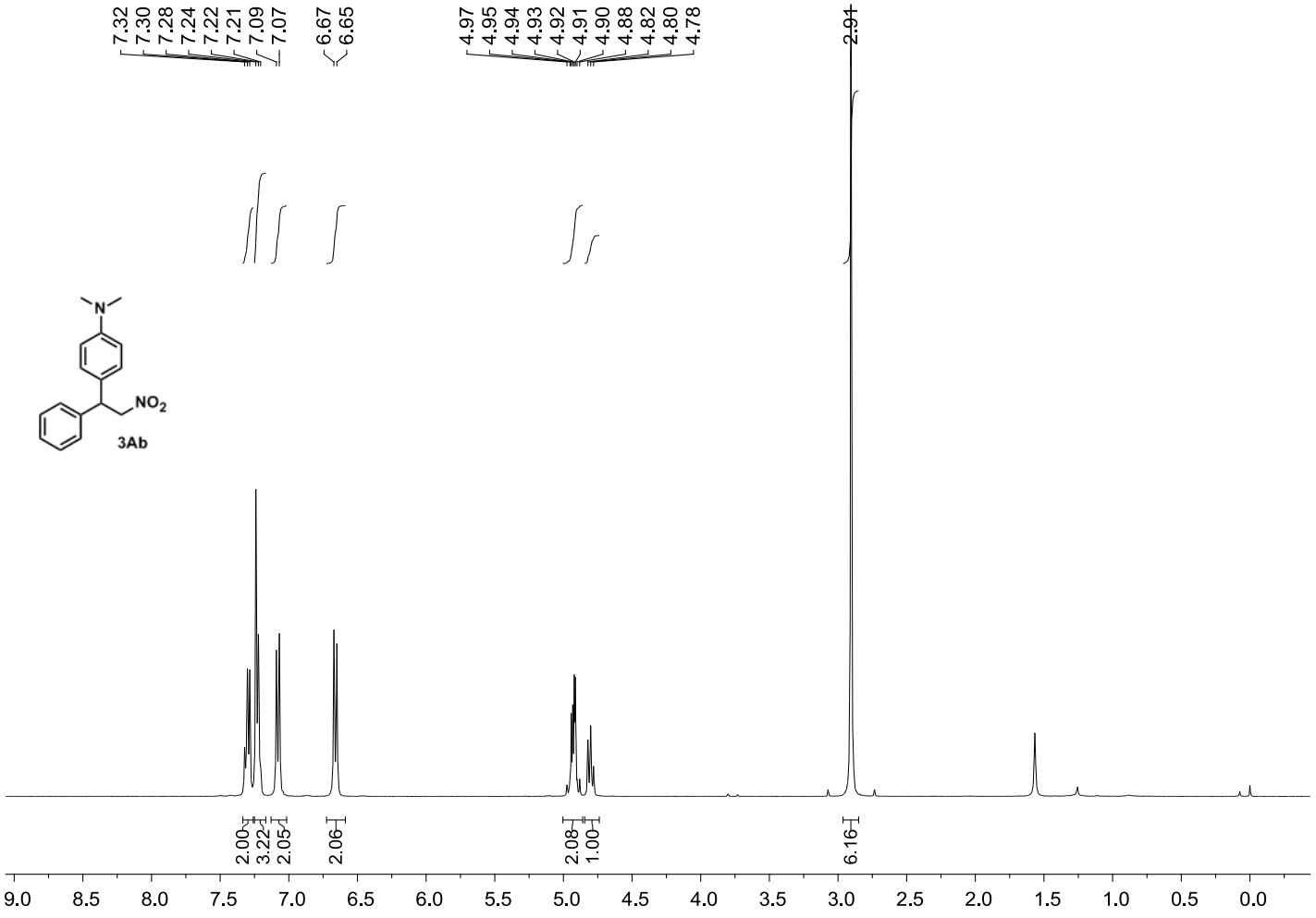


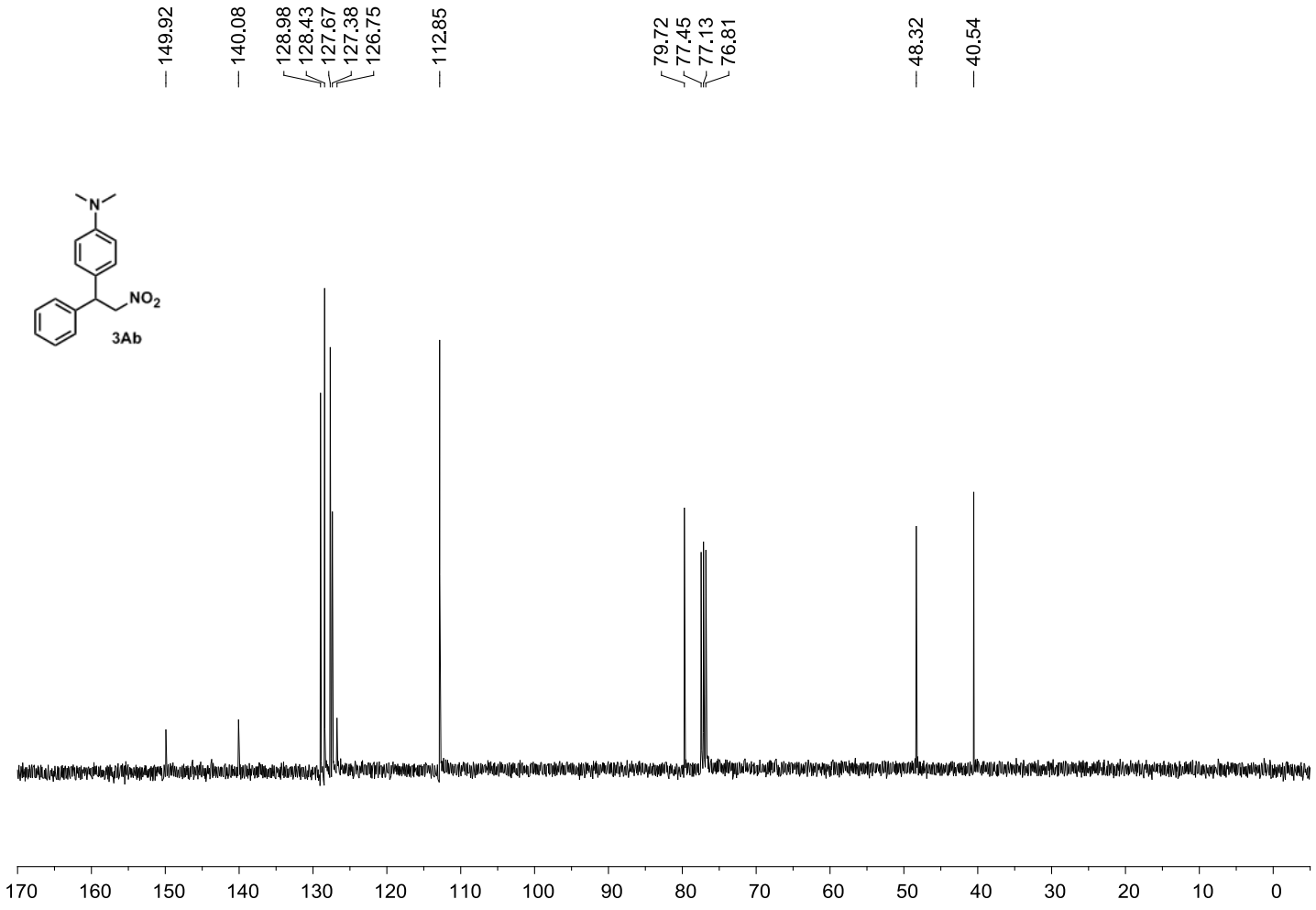


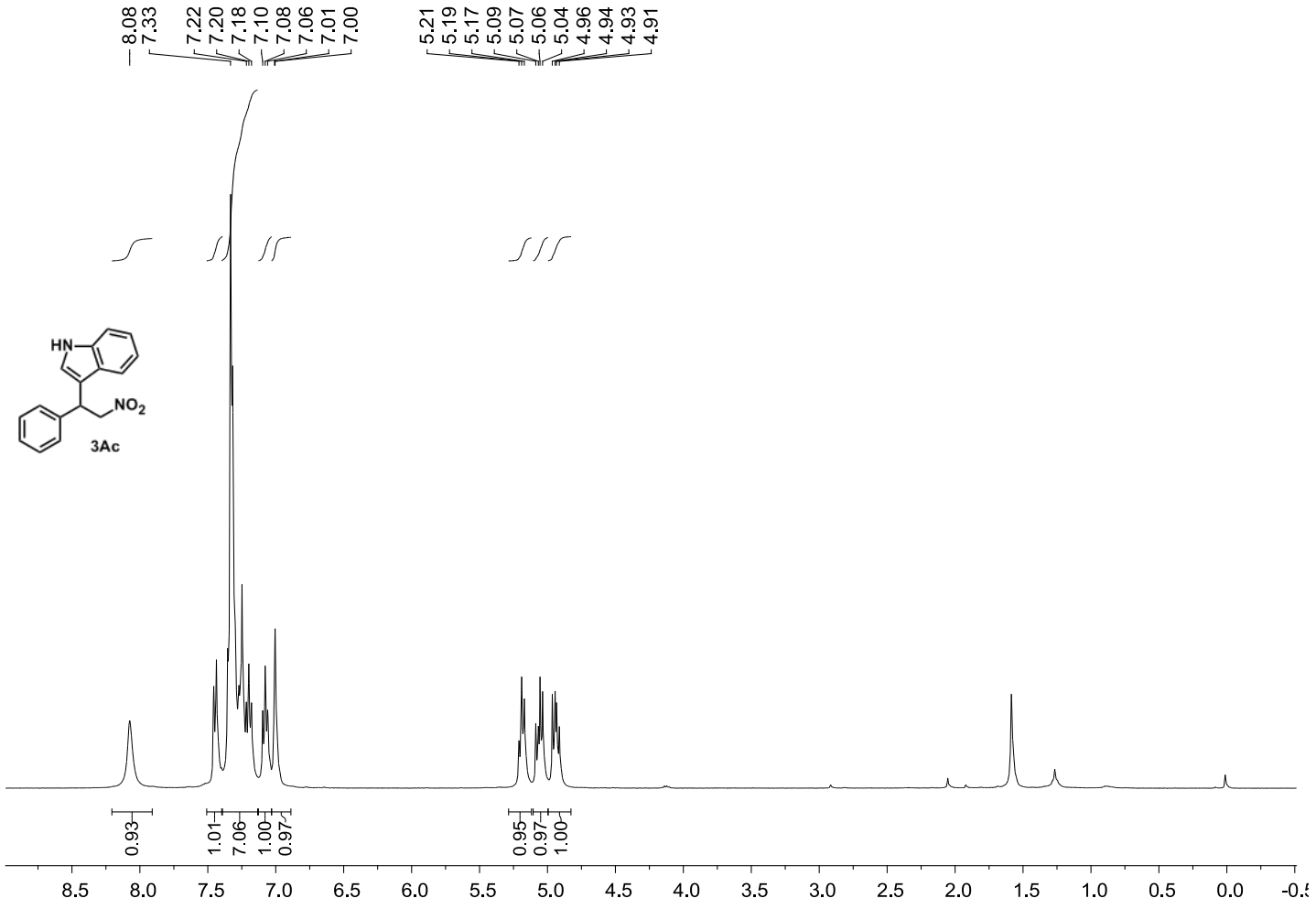


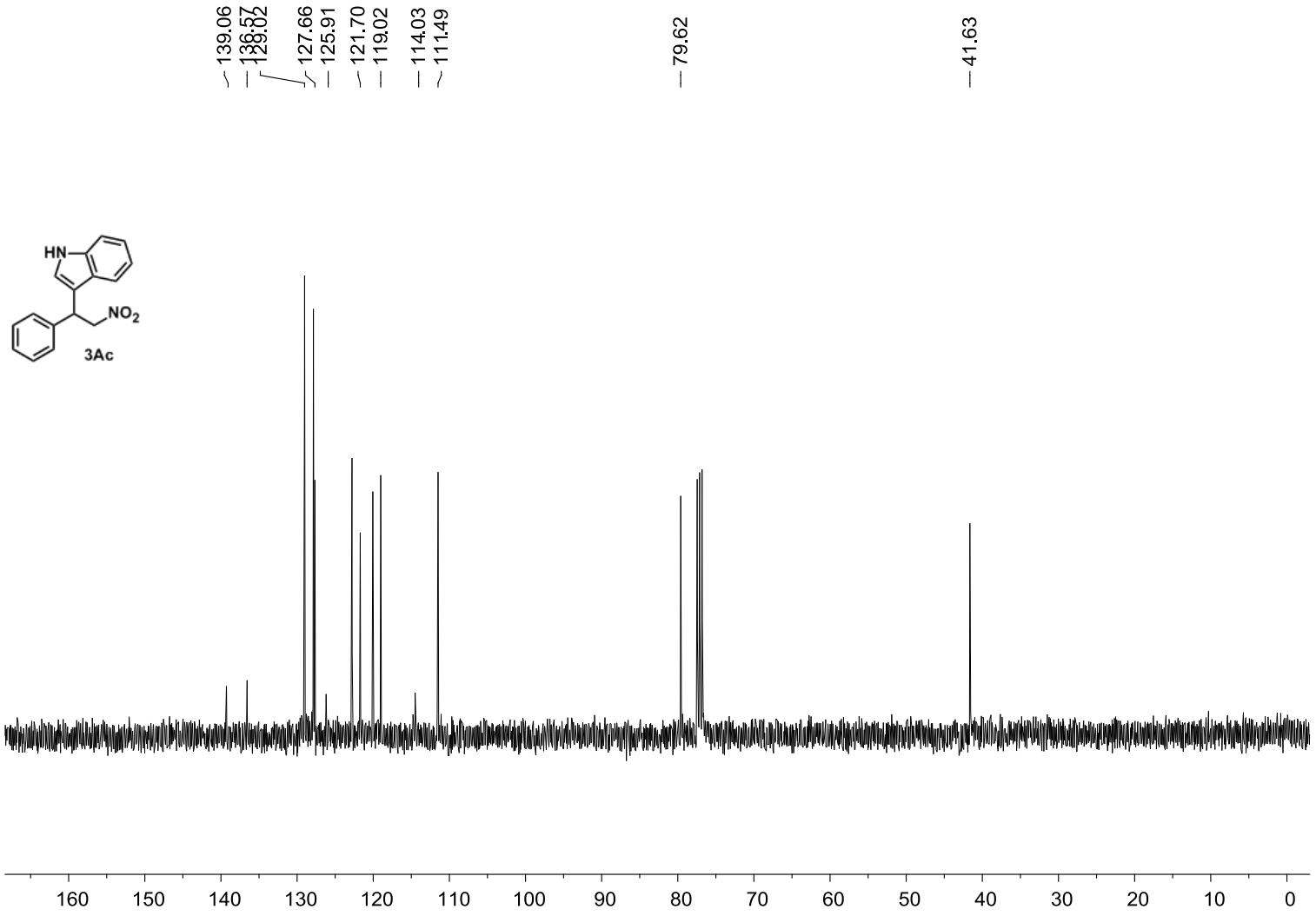


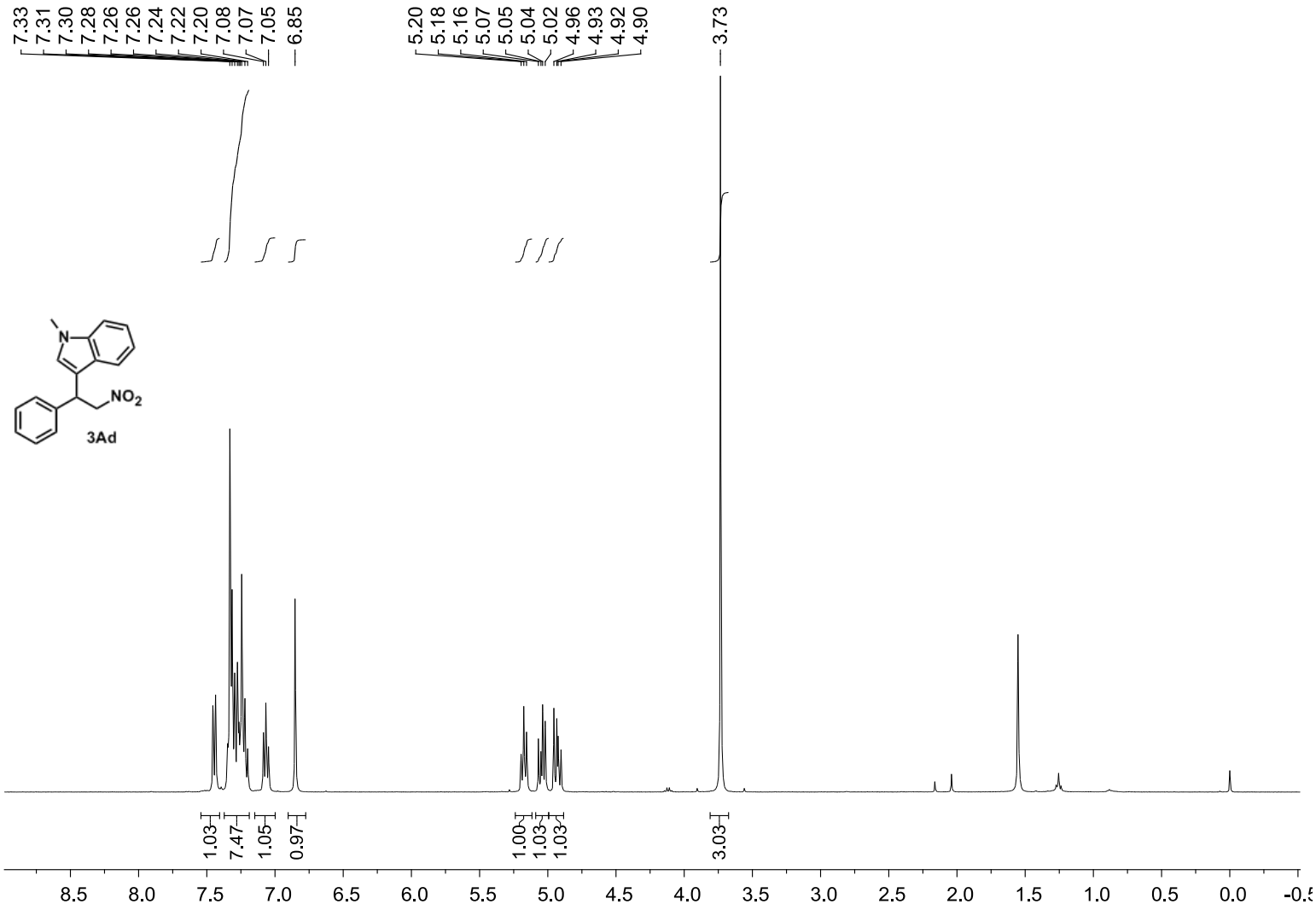


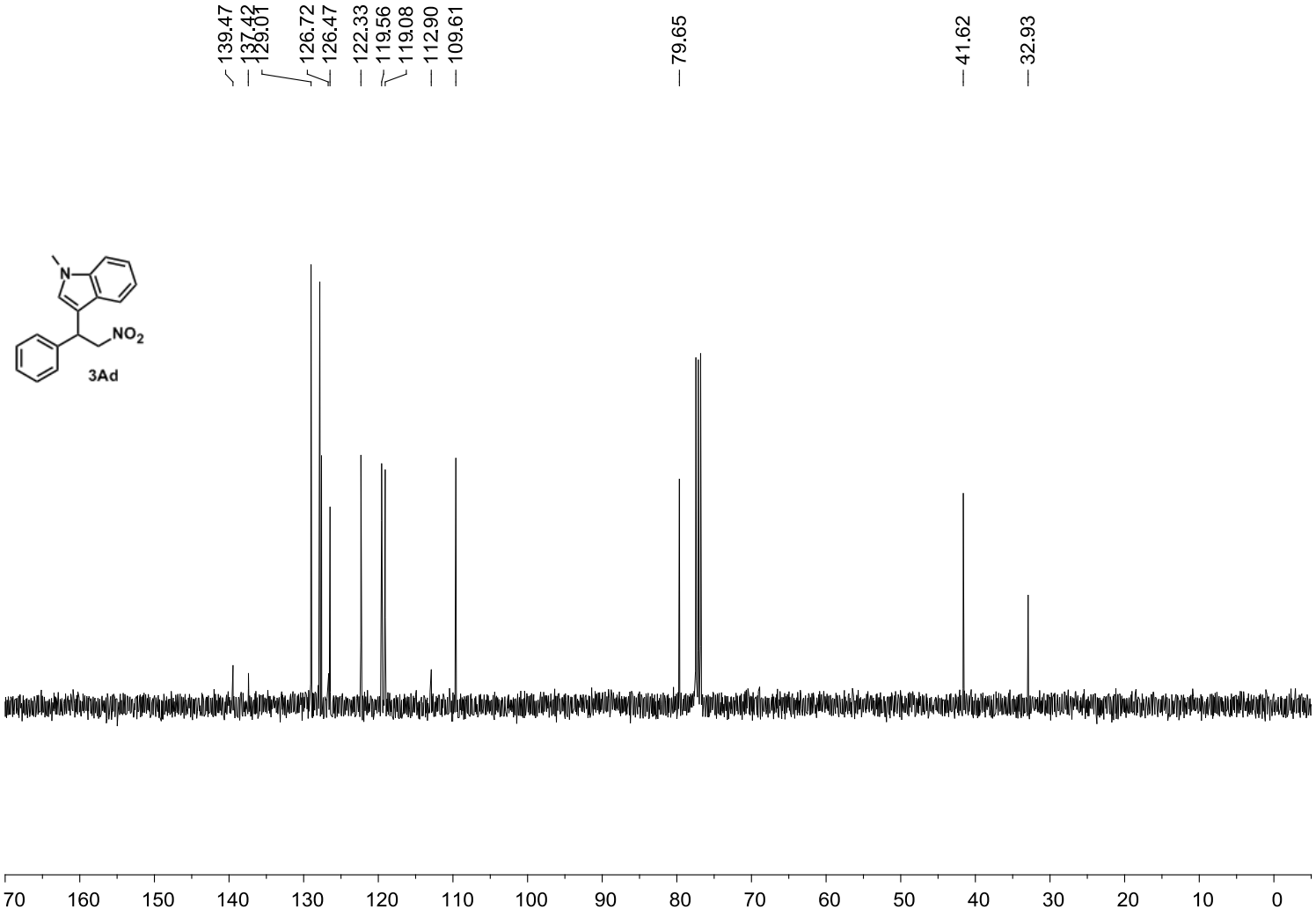








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119.08
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109.61
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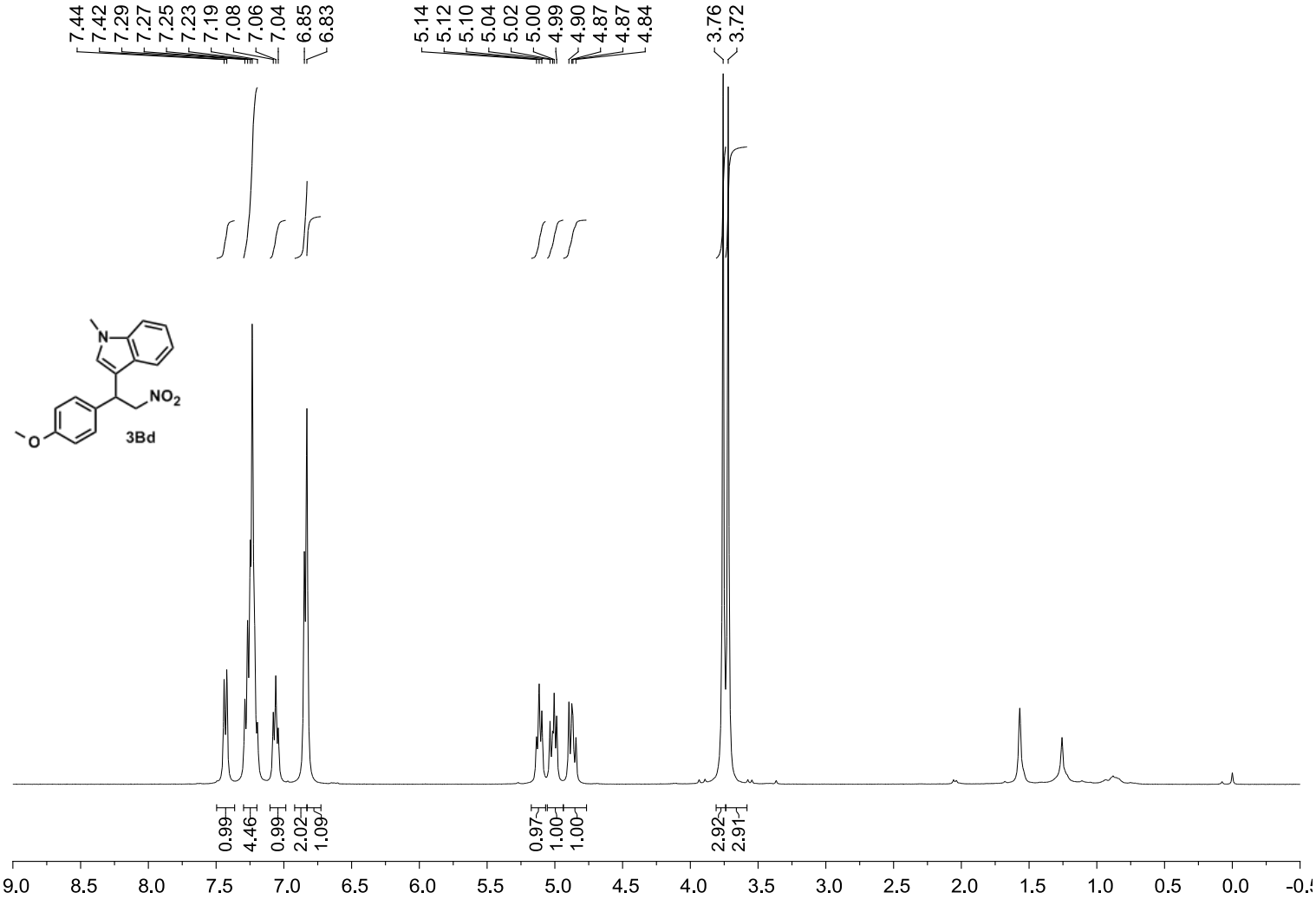

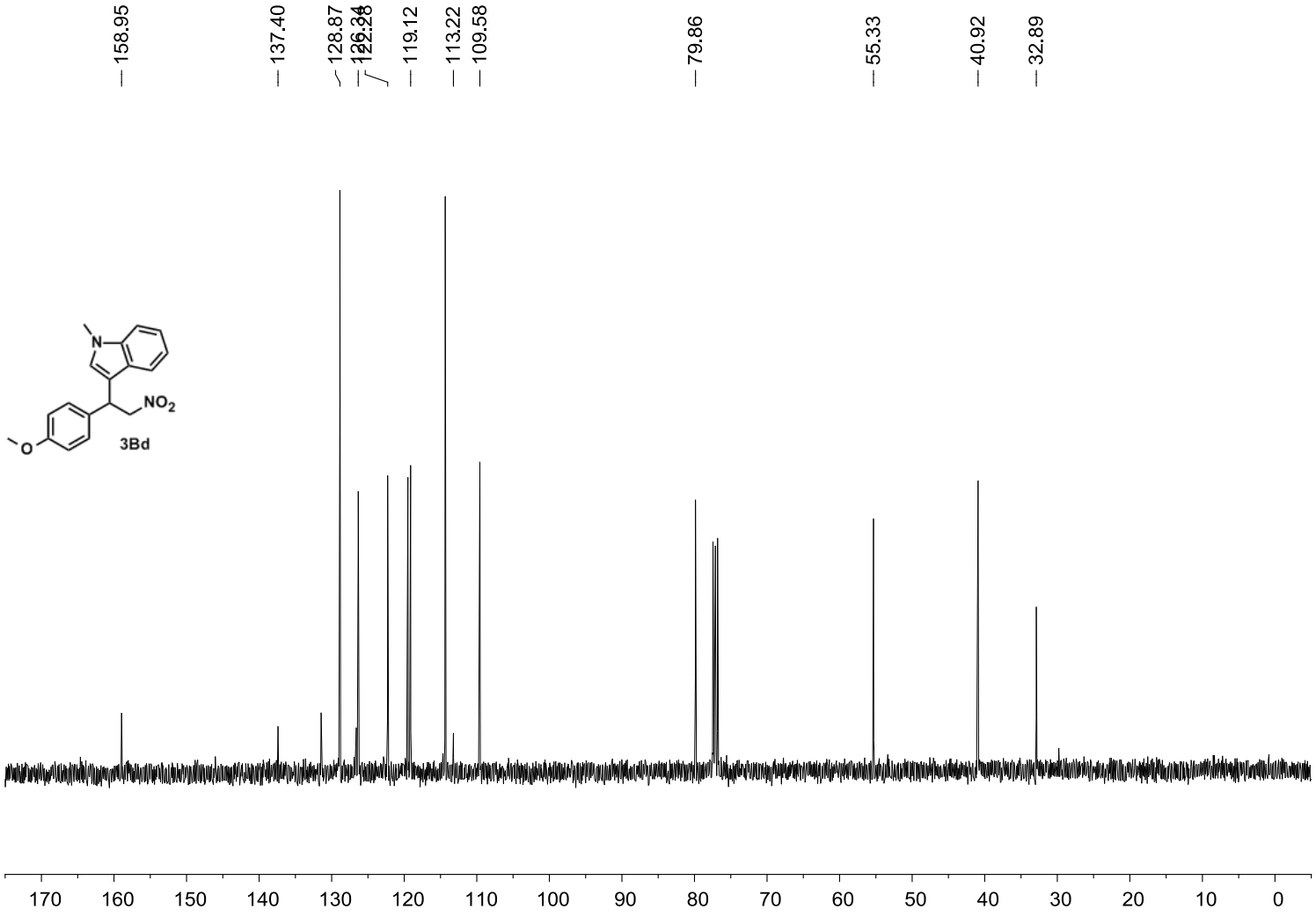

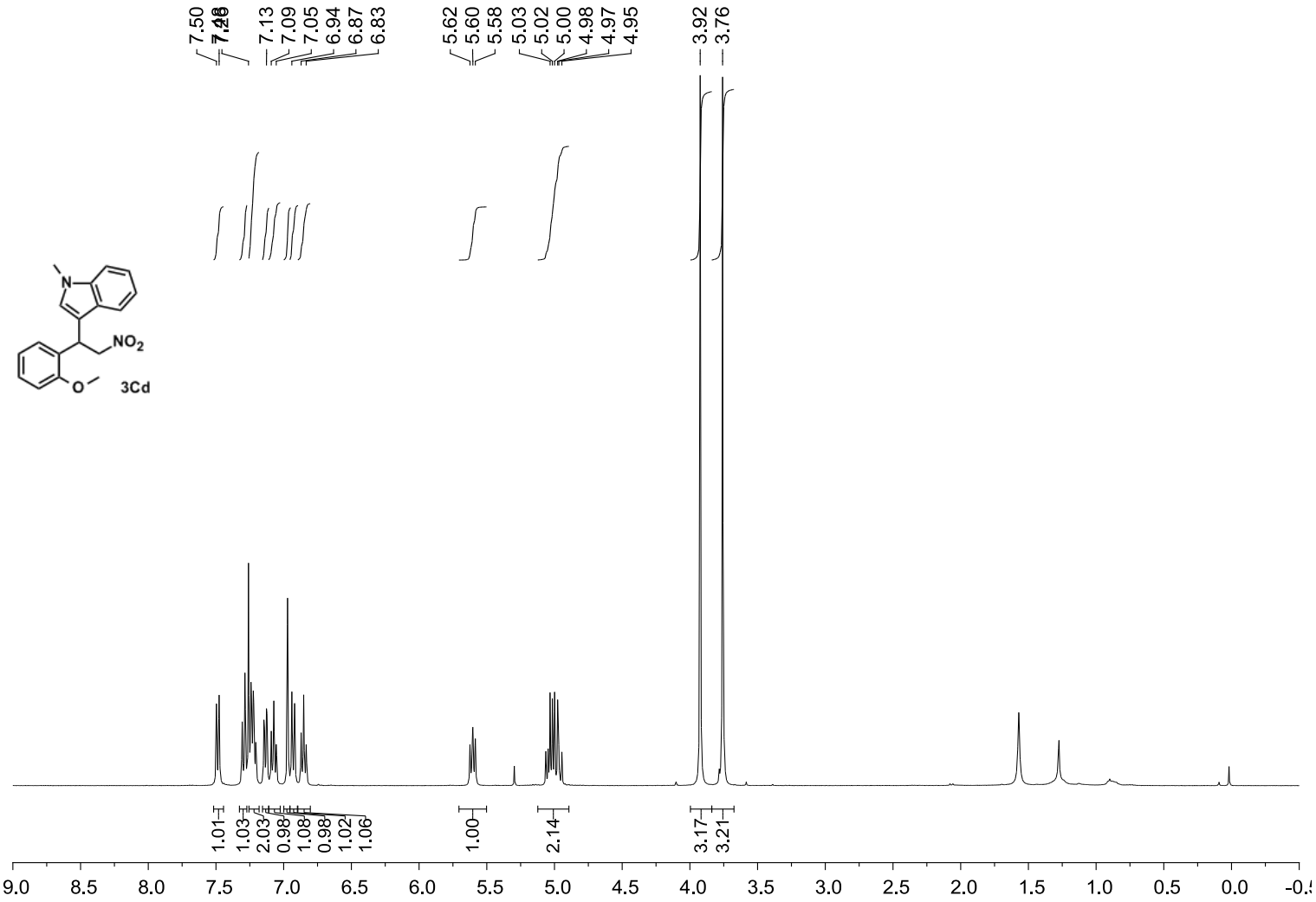

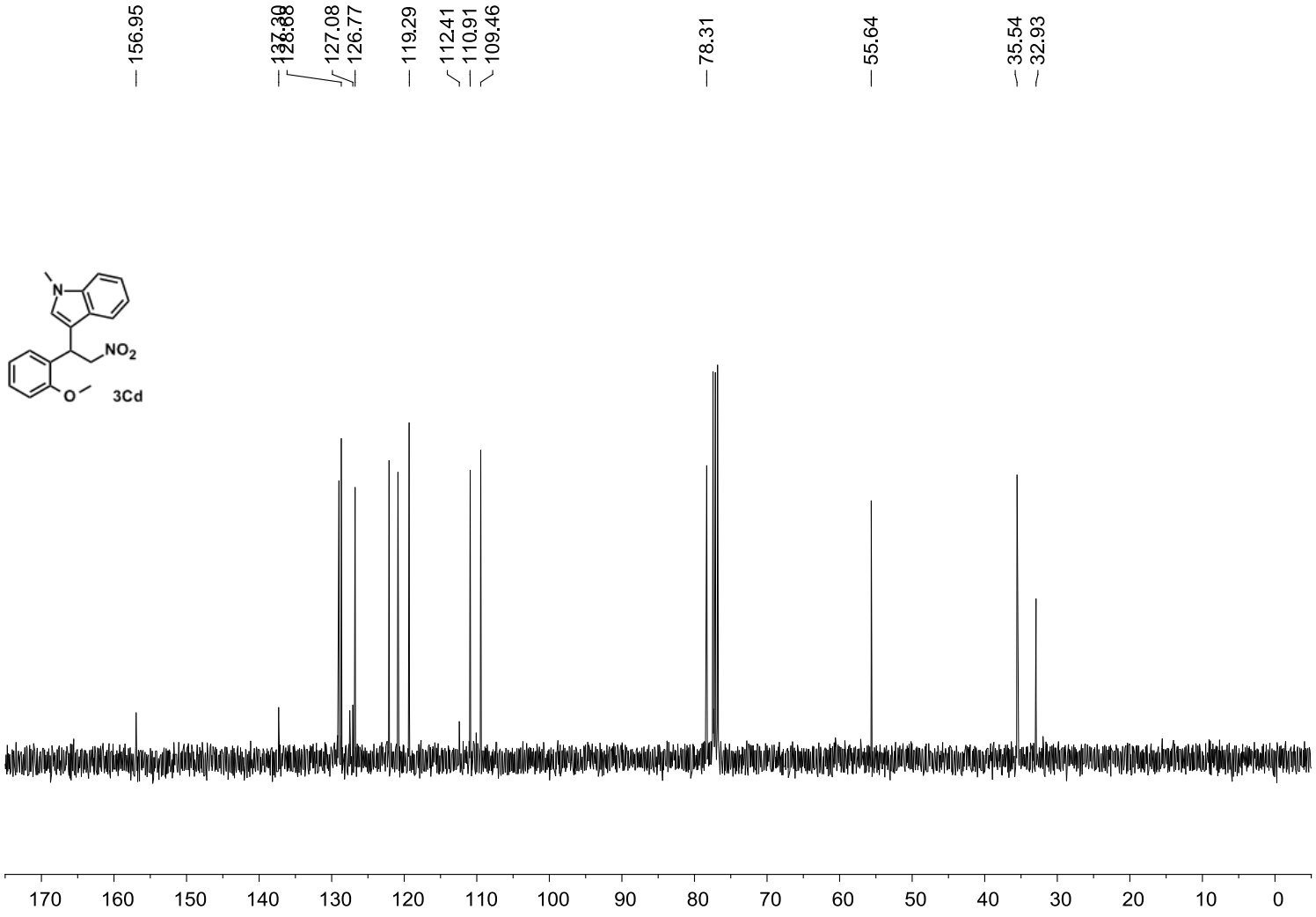

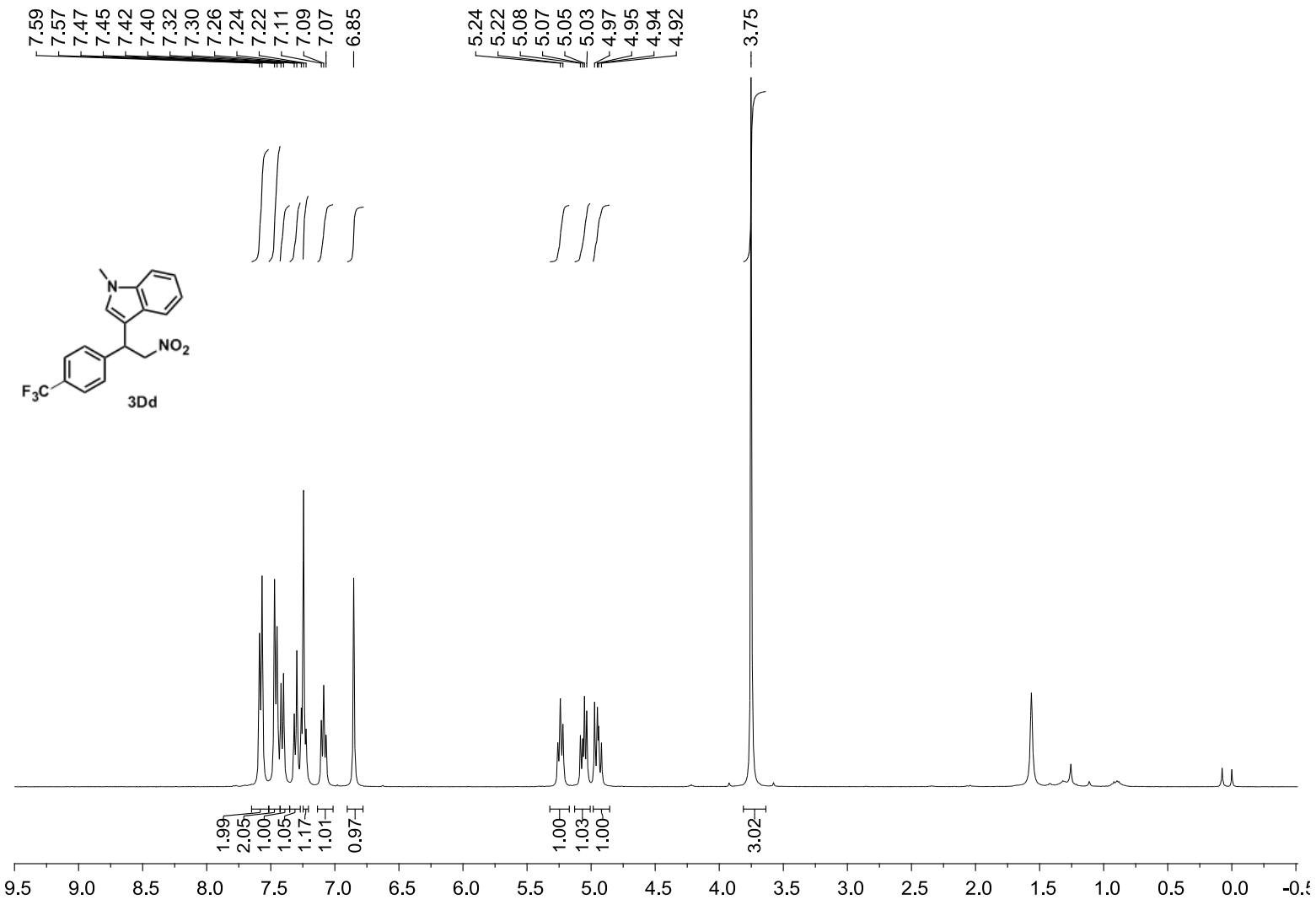

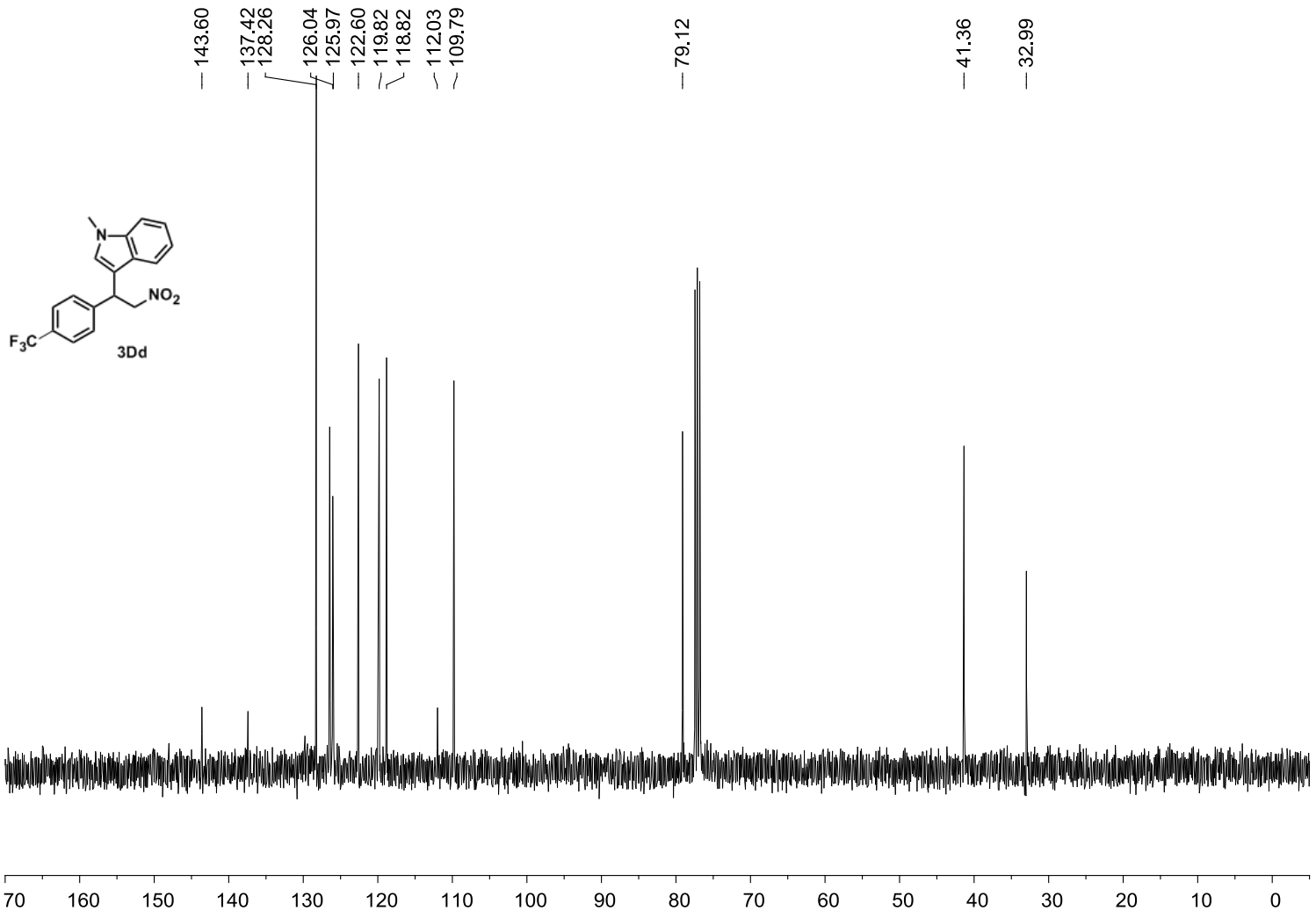

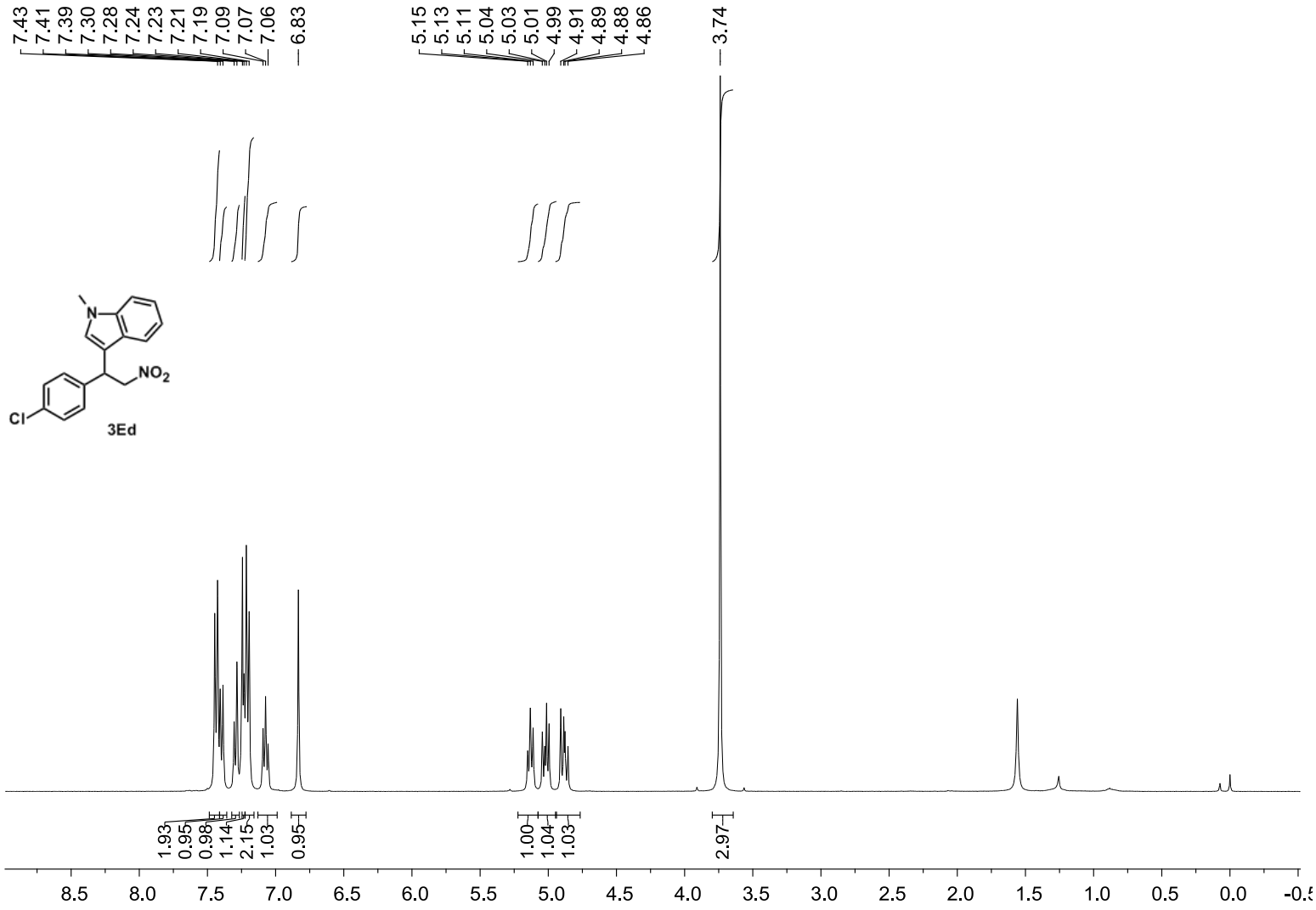
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7.19
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7.06
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5.15
5.13
5.11
5.04
5.03
5.01
4.99
4.91
4.89
4.88
4.86
3.74
NO2
Cl
3Ed
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0.95
0.98
1.14
2.15
1.03
0.95
1.00
1.04
1.03
2.97
8.5
8.0
7.5
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6.0
5.5
5.0
4.5
4.0
3.5
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1.0
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