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Supporting Information

Regioselective nitration of Anilines with $Fe(NO_3)_3 \cdot 9H_2O$ as Promoter and Nitro Source

Yang Gao,* Yuanyou Mao, Biwei Zhang, Yingying zhan, Yanping Huo*

School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, 510006, China
Website: www.gdutyphuo.com, E-mail: gaoyang@gdut.edu.cn

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A. Experimental Procedures

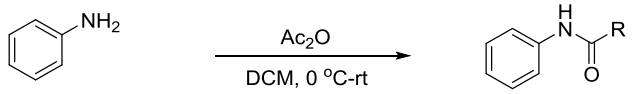
I. General Methods

^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz and ^{13}C NMR spectra were recorded in $CDCl_3$ at 100 MHz. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, and chloroform is used as a solvent with TMS as the internal standard. GC–MS was obtained using electron ionization. HRMS was carried out on a MAT 95XP (Thermo). TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm.

II. General Procedure for Synthesis of the Substrates

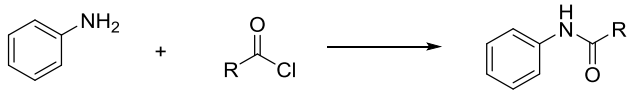
All the anilines used in this work were commercially available. The *N*-phenylacetamides were synthesized according to the reported method.

1. Preparation of *N*-phenylacetamides (1)[1]:



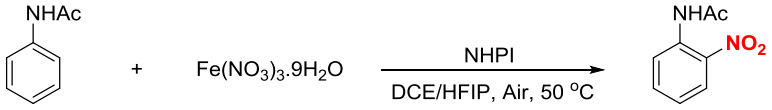
In a 50 mL round bottom flask, anilines (5.0 mmol, 1.0 equiv) was dissolved in 20 mL of dichloromethane under argon atmosphere. Then, acetic anhydride (6.0 mmol, 1.2 equiv) was added drop wise and the reaction was stirred at room temperature till complete consumption of anilines. After completion of the reaction, the mixture was washed with a saturated solution of sodium carbonate, the organic layer dried with Na_2SO_4 and the solvent removed under reduced pressure to obtain the desider acetaniline in quantative yield. In most cases analytically pure acetanilines can be obtained after extraction however if necessary purification by flash chromatography with ethyl acetate/hexane was used.

2. Preparation of *N*-phenylacetamides (2)[2]:



The amine (7.6 mmol) was dissolved in 15 mL of CH_2Cl_2 and cooled to 0 °C using an ice bath. NEt_3 (8.36 mmol, 1.1 equiv) was added to the amine solution followed by the corresponding acid chloride (7.6 mmol, 1.00 equiv) drop-wise over 30 min. Then the mixture was stirred for 3-24 h at room temperature. The mixture was then poured into a separatory funnel and washed with 3×40.0 mL of saturated $NaHCO_3$ (aq) followed by washing with 50.0 mL of saturated NaCl (aq). The organic layer was then dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude amide was obtained in 90-98% yield. The product suitable for hydrogenation was obtained from distillation (liquid amides), trituration in n-hexanes or from recrystallization using EtOH as a recrystallization solvent (solid amides).

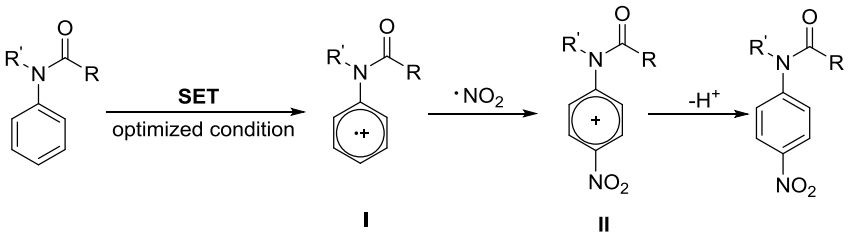
III. General Procedure for $Fe(NO_3)_3{\cdot}9H_2O$ promoted *ortho*-nitration reaction of aniline derivatives.



1a **2a**

N-phenylacetamide **1a** (0.3 mmol), $Fe(NO_3)_3{\cdot}9H_2O$ (0.45 mmol) and NHPI (0.06 mmol) in DCE:HFIP (10:1, 2 mL) were added to a tube equipped with magnetic stirrer bar. The reaction was under air and the mixture was stirred at 50 °C (oil bath temperature) for the desired reaction time (10 h). After the reaction was finished (monitored by TLC), the mixture was cooled to room temperature and quenched with aqueous NaCl, and the crude product was extracted with ethyl acetate. The organic extracts were concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel with light petroleum ether/ethyl acetate as eluent to afford the desired product.

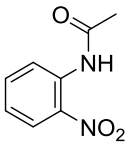
B. Plausible Mechanism for *para*-Nitration



The formation of *para*-nitration product may go through a different cationic radical pathway. Firstly, SET between the *N*-methyl-*N*-phenylacetamide and the Fe(III) center generated the cationic radical species **I**. Next, NO_2• was generated from $Fe(NO_3)_3$ under thermal condition and reacted with **I** to deliver intermediate **II**. Complex **II** underwent deprotonation to provide the *para*-nitration product.

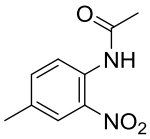
C. Characterization Data for Compounds 2a-2z', 2aa, 2ab and 4-6

***N*-(2-Nitrophenyl)acetamide (2a)**[3]



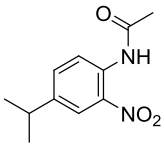
White solid (44.3 mg, 82%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.33 (s, 1H), 8.76 (d, J = 8.5 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 7.8 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 136.3, 136.0, 134.8, 125.7, 123.2, 122.2, 25.6.

***N*-(4-Methyl-2-nitrophenyl)acetamide (2b)**[3]



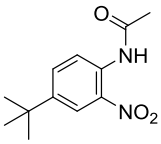
White solid (29.1 mg, 50%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.59 (d, J = 8.6 Hz, 1H), 7.97 (s, 1H), 7.43 (d, J = 8.5 Hz, 1H), 2.36 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 136.7, 136.1, 133.4, 132.3, 125.4, 122.0, 25.4, 20.4.

***N*-(4-*iso*-Propyl-2-nitrophenyl)acetamide (2b)**[4]



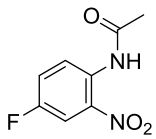
White solid (48.0 mg, 72%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.62 (d, *J* = 8.7 Hz, 1H), 8.02 (s, 1H), 7.51 (d, *J* = 8.6 Hz, 1H), 2.94 (dt, *J* = 13.7, 6.9 Hz, 1H), 2.27 (s, 3H), 1.26 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 144.4, 136.4, 134.4, 132.5, 122.9, 122.3, 33.3, 25.5, 23.5.

***N*-(4-(tert-Butyl)-2-nitrophenyl)acetamide (2c)**[5]



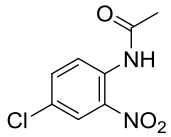
White solid (56.6 mg, 80%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.62 (d, J = 8.9 Hz, 1H), 8.16 (s, 1H), 7.67 (d, J = 8.8 Hz, 1H), 2.27 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 146.9, 136.2, 133.4, 132.2, 122.1, 122.0, 34.5, 30.9, 25.5.

***N*-(4-Fluoro-2-nitrophenyl)acetamide (2e)**[4]



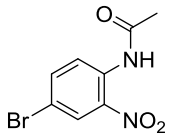
White solid (44.6 mg, 75%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.79 (dd, J = 9.4, 5.2 Hz, 1H), 7.92 (dd, J = 8.4, 2.6 Hz, 1H), 7.40 (dd, J = 11.5, 4.7 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 156.9 (d, *J* = 247.7 Hz), 141.7 (d, *J* = 130.1 Hz), 131.4 (d, *J* = 3.0 Hz), 124.1 (d, *J* = 7.3 Hz), 123.4 (d, *J* = 22.0 Hz), 112.2 (d, *J* = 27.2 Hz), 25.47. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.02.

_N_-(4-Chloro-2-nitrophenyl)acetamide (2f)[3]



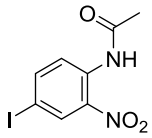
White solid (38.5 mg, 60%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.77 (d, J = 9.1 Hz, 1H), 8.19 (s, 1H), 7.59 (d, J = 11.2 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 136.3, 135.9, 133.5, 128.3, 125.3, 123.4, 25.6.

_N_-(4-Bromo-2-nitrophenyl)acetamide (2g)[3]



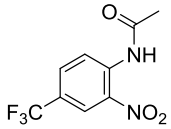
White solid (63.5 mg, 82%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.70 (d, J = 9.1 Hz, 1H), 8.32 (s, 1H), 7.71 (d, J = 9.1 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 138.7, 136.5, 133. 9, 128.4, 123.5, 115.2, 25.6.

_N_-(4-Iodo-2-nitrophenyl)acetamide (2h)[6]



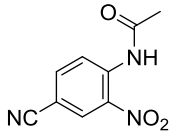
White solid (71.6 mg, 78%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.54 (d, J = 9.0 Hz, 1H), 8.47 (s, 1H), 7.87 (d, J = 10.7 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 144.4, 136.5, 134.6, 133.9, 123.6, 84.6, 25.6.

_N_-(2-Nitro-4-(trifluoromethyl)phenyl)acetamide (2i)[7]



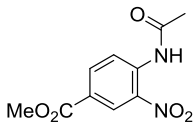
White solid (48.4 mg, 65%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.48 (s, 1H), 8.99 (d, J = 8.9 Hz, 1H), 8.50 (s, 1H), 7.86 (d, J = 8.9 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 137.6, 135.3, 132.3 (q, *J* = 3.2 Hz), 124.6 (d, *J* = 99.2 Hz), 123.4 (q, *J* = 4.1 Hz), 122.6, 121.4, 25.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.68.

_N_-(4-Cyano-2-nitrophenyl)acetamide (2j)[9]



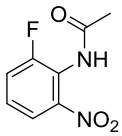
White solid (25.8 mg, 42%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 9.03 (d, J = 8.9 Hz, 1H), 8.55 (d, J = 1.6 Hz, 1H), 7.87 (m, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 142.3, 138.38, 135.35, 130.13, 122.66, 116.52, 106.78, 25.74.

Methyl 4-acetamido-3-nitrobenzoate (2k)



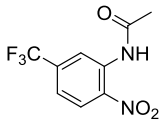
White solid (35.7 mg, 50%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 8.90 (d, J = 8.9 Hz, 1H), 8.87 (d, J = 1.8 Hz, 1H), 8.25 (dd, J = 8.9, 1.6 Hz, 1H), 3.95 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 164.6, 138.2, 136.5, 135.5, 127.5, 124.9, 121.6, 52.6, 25.7. ESI-HRMS calcd for $C_{10}H_{11}N_2O_5$ $(M + H)^+$ 239.0662; found, 239.0667.

***N*-(2-Fluoro-6-nitrophenyl)acetamide (2l)**[8]



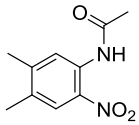
White solid (29,7 mg, 80%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.78 (dd, J = 9.3, 5.2 Hz, 1H), 7.91 (d, J = 10.8 Hz, 1H), 7.39 (t, J = 9.1 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 156.9 (d, *J* = 247.7 Hz), 136.4 (d, *J* = 9.6), 131.3 (d, *J* = 2.8 Hz), 124.1 (d, *J* = 7.2 Hz), 123.4 (d, *J* = 22.0 Hz), 112.2 (d, *J* = 27.2 Hz), 25.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.03.

***N*-(2-Nitro-5-(trifluoromethyl)phenyl)acetamide (2m)**[7]



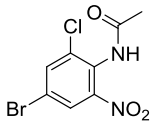
White solid (44.6 mg, 60%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 9.16 (s, 1H), 8.32 (d, J = 8.8 Hz, 1H), 7.42 (d, J = 8.7 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 137.6, 137.1 (d, *J* = 33.5 Hz), 136.6, 135.22, 126.45, 122.6 (d, *J* = 266.8 Hz), 119.6 (q, *J* = 3.5 Hz), 25.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.65.

***N*-(4,5-Dimethyl-2-nitrophenyl)acetamide (2n)**[10]



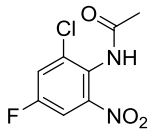
White solid (48.7 mg, 78%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.47 (s, 1H), 7.89 (s, 1H), 2.29 (s, 3H), 2.23 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 146.6, 134.0, 132.6, 132.2, 125.7, 122.4, 25.4, 20.3, 18.9.

***N*-(4-Bromo-2-chloro-6-nitrophenyl)acetamide (2o)**



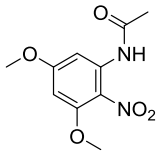
White solid (45.6 mg, 52%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.84 (s, 1H), 7.71 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 146.0, 136.7, 132.6, 127.5, 126.8, 118.9, 23.5. ESI-HRMS calcd for $C_8H_7BrClN_2O_3$ $(M + H)^+$ 292.9323; found, 292.9332.

***N*-(2-Chloro-4-fluoro-6-nitrophenyl)acetamide (2p)**[11]



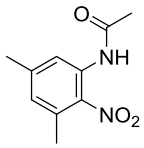
White solid (31.3 mg, 45%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.62 (d, J = 5.3 Hz, 1H), 7.48 (d, J = 7.1 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 158.9 (d, *J* = 253.9 Hz), 146.4 (d, *J* = 6.6 Hz), 133.6 (d, *J* = 11.2 Hz), 125.1 (d, *J* = 4.3 Hz), 121.9 (d, *J* = 25.1 Hz), 111.7 (d, *J* = 27.0 Hz), 23.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.13.

***N*-(3,5-Dimethoxy-2-nitrophenyl)acetamide (2q)**[3]



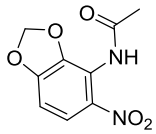
White solid (33.1 mg, 46%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.70 (s, 1H), 6.27 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 163.5, 155.4, 135.3, 134.3, 97.7, 95.7, 56.6, 55.9, 14.1.

***N*-(3,5-Dimethyl-2-nitrophenyl)acetamide (2r)**



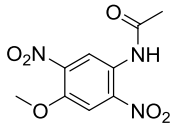
White solid (30.0 mg, 48%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.96 (s, 1H), 6.86 (s, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 143.4, 139.3, 133.0, 131.3, 128.1, 121.8, 25.0, 21.6, 19.7. ESI-HRMS calcd for $C_{10}H_{13}N_2O_3$ $(M + H)^+$ 209.0920; found, 209.0926.

_N_-(5-Nitrobenzo[d][1,3]dioxol-4-yl)acetamide (2s)



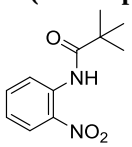
White solid (40.3 mg, 60%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.36 (s, 1H), 7.65 (s, 1H), 6.10 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 154.3, 143.3, 133.9, 104.6, 103.1, 101.3, 29.7, 25.7. ESI-HRMS calcd for $C_9H_9N_2O_5$ $(M + H)^+$ 225.0505; found, 225.0512.

_N_-(4-Methoxy-2,5-dinitrophenyl)acetamide (2t)



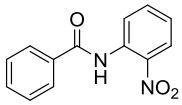
White solid (50.5 mg, 66%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 9.21 (s, 1H), 7.86 (s, 1H), 4.00 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 146.8, 137.6, 128.3, 119.1, 115.4, 109.9, 57.1, 25.3. ESI-HRMS calcd for $C_9H_{10}N_3O_6$ $(M + H)^+$ 256.0564; found, 256.0569.

_N_-(2-Nitrophenyl)pivalamide (2u)[12]



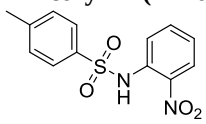
White solid (59.9 mg, 90%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.73 (s, 1H), 8.82 (d, J = 8.5 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 136.3, 136.0, 135.4, 125.7, 122.9, 122.1, 27.4.

_N_-(2-Nitrophenyl)benzamide (2v)[3]



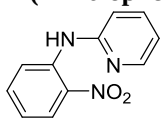
White solid (39.9 mg, 55%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.35 (s, 1H), 9.01 (d, J = 8.5 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 7.3 Hz, 2H), 7.71 (t, J = 7.8 Hz, 1H), 7.61 (t, J = 7.3 Hz, 1H), 7.54 (t, J = 7.4 Hz, 2H), 7.22 (t, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ165.7, 136.4, 136.2, 135.3, 134.0, 132.6, 129.0, 127.3, 125.9, 123.3, 122.1.

4-Methyl-_N_-(2-nitrophenyl)benzenesulfonamide (2w)[13]



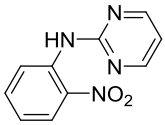
White solid (70.1 mg, 80%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.51 (t, J = 7.8 Hz, 1H), 7.19 (d, J = 7.9 Hz, 2H), 7.08 (t, J = 7.8 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 137.0, 135.8, 135.7, 134.0, 130.0, 127.2, 126.1, 123.7, 121.0, 21.6.

_N_-(2-Nitrophenyl)pyridin-2-amine (2x)[14]



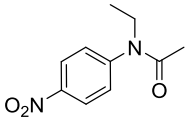
White solid (38.7 mg, 60%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.75 (d, J = 8.7 Hz, 1H), 8.35 (s, 1H), 8.23 (d, J = 8.5 Hz, 1H), 7.65 (t, J = 8.1 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 6.96 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 147.9, 138.9, 138.0, 135.7, 134.7, 126.2, 119.7, 119.6, 117.8, 113.8.

_N_-(2-Nitrophenyl)pyrimidin-2-amine (2y)[14]



White solid (37.6 mg, 58%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 8.91 (d, J = 8.6 Hz, 1H), 8.47 (d, J = 4.7 Hz, 2H), 8.17 (d, J = 8.4 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 6.98 (t, J = 7.7 Hz, 1H), 6.84 (t, J = 4.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 136.9, 135.6, 135.4, 126.1, 120.9, 120.8.

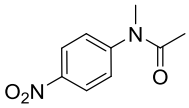
_N_-Ethyl-_N_-(4-nitrophenyl)acetamide (2z)



p:o = 5:2

White solid (38.7 mg, 62%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 3.80 (q, J = 6.9 Hz, 2H), 1.93 (s, 3H), 1.13 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.2, 148.6, 146.6, 136.0, 134.0, 132.1, 129.4, 128.8, 125.5, 125.0, 99.9, 44.4, 44.1, 23.0, 22.8, 13.3, 13.0. ESI-HRMS calcd for $C_{10}H_{13}N_2O_3$ $(M + H)^+$ 209.0920; found, 209.0915.

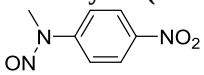
_N_-Methyl-_N_-(4-nitrophenyl)acetamide (2z')[3]



p:o = 5:2

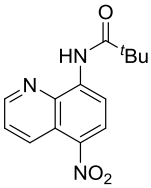
White solid (34.9 mg, 60%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 2H), 7.40 (s, 2H), 3.33 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 169.9, 149.9, 137.6, 134.4, 134.1, 130.9, 129.4, 129.3, 127.3, 125.5, 125.0, 37.3, 36.7, 22.6, 22.0.

_N_-Methyl-_N_-(4-nitrophenyl)nitrous amide (2aa)[16]



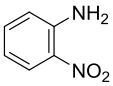
Colorless oil (38.0 mg, 70%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 9.1 Hz, 2H), 7.76 (d, J = 9.1 Hz, 2H), 3.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 145.9, 125.2, 117.8, 30.0.

_N_-(5-Nitroquinolin-8-yl)pivalamide (2ab)[17]



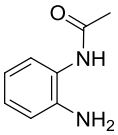
White solid (45.1 mg, 55%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 9.28 (d, J = 8.7 Hz, 1H), 8.92 (d, J = 3.7 Hz, 1H), 8.86 (d, J = 8.8 Hz, 1H), 8.55 (d, J = 8.8 Hz, 1H), 7.72 (dd, J = 8.8, 4.1 Hz, 1H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 149.0, 141.0, 138.4, 137.7, 133.3, 127.9, 124.6, 121.8, 113.4, 40.7, 27.6.

2-Nitroaniline (4)[3]



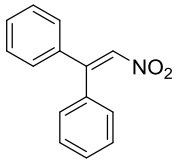
Colorless oil (33.1 mg, 80%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H), 6.70 (t, J = 7.7 Hz, 1H), 6.08 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 135.6, 132.3, 126.2, 118.7, 116.9.

_N_-(2-Aminophenyl)acetamide (5)



Yellow solid (32.4 mg, 72%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (m, 7H), 7.29 (m, 2H), 7.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 137.1, 135.5, 134.4, 130.9, 129.3, 128.9, 128.9, 128.8, 128.5.

(2-Nitroethene-1,1-diyl)dibenzene (6)



White solid (48.6 mg, 36%), ^{1}H NMR (400 MHz, DMSO) δ 9.15 (s, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.57 (t, *J* = 7.5 Hz, 1H), 4.85 (s, 2H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 168.9, 142.5, 126.3, 125.9, 124.1, 116.7, 116.4, 23.8.

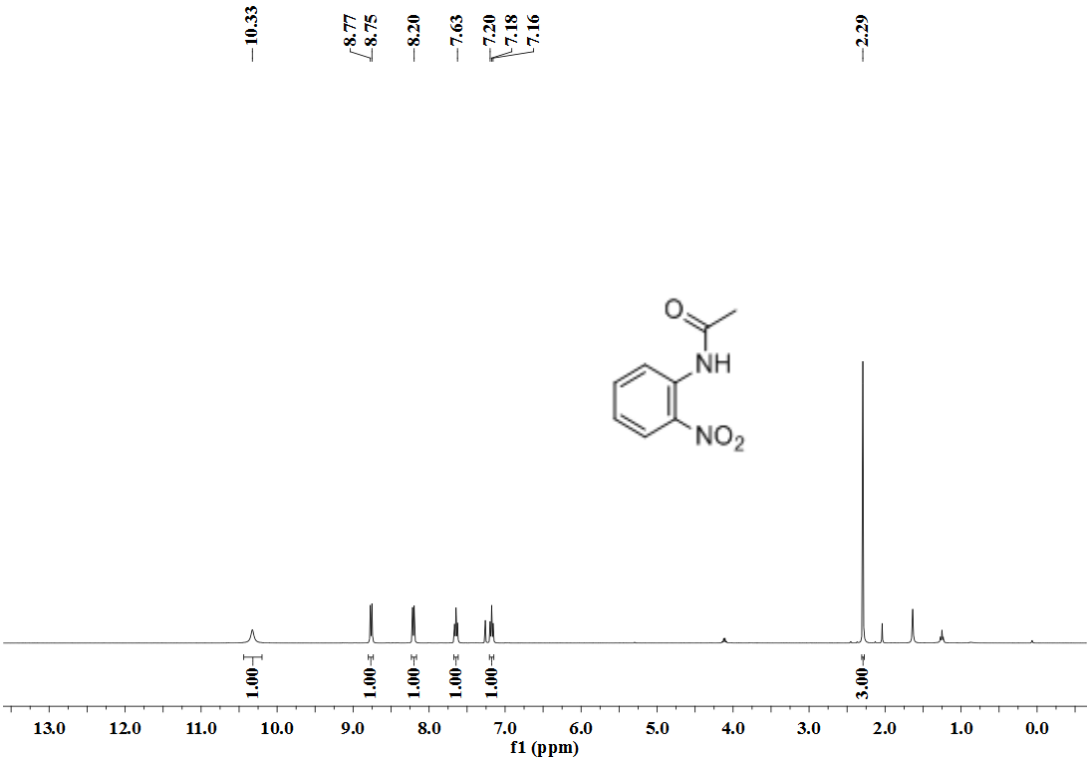
D. References

1. B. Wang, C. Jiang, J. Qian, S. Zhang, X. Jia and Y. Yuan, *Org. Biomol.Chem*, 2018, **16**, 101.
2. J.M. John, R. Loorthuraja, E. Antoniuk, S.H. Bergens, *Catal. Sci. Technol.* 2015, **5**, 1181.
3. Y. Lu, Y. Li, R. Zhang, K. Jin and C. Duan, *Tetrahedron* 2013, **69**, 9422.
4. D. Xie, Y. Wang, J. Xie, J. Lu, J. Cui, M. Zhang, L. Fu, Y. Wang, *Med. Chem. Res.* 2014, **23**, 4977.
5. D. Frantz, A. Linden, K. Baldridge, J. Siegel, *J. Am. Chem. Soc.* 2012, **134**, 1528.
6. B. Krassowska-Swiebocka, G. Prokopienko, L. Skulski, *Molecules* 2005, **10**, 394.
7. G. Navarrete-Vázquez, M. Rojano-Vilchis, *Eur. J. Med. Chem.* 2006**, 41**, 135.
8. A. Bedernjak, A. Zaytsev, M. Babolat, M. Cellier, A. James, S. Orenga, J. Perry, P. Groundwater, R. Anders, *J. Med. Chem.* 2016, **59**, 4476.
9. P. Mani, A. Singh, S. Awasthi, *Tetrahedron Letters* 2014, **55**, 1879.
10. Y. Jia, F. Gou, R. Fang, H. Jing and Z. Zhu, *Chin. J. Chem.* 2014, **32**, 513.
11. C. Mo, Z. Zhang, C. Guise, X. Li, J. Luo, Z. Tu, Y. Xu, A. Patterson, J. Smaill, X. Ren, X. Lu, K. Ding, *ACS Med. Chem. Lett.* 2017, **8**, 543.
12. Y. Ji, H. Yan and Q. Jiang, *Eur. J. Org. Chem*. 2015, 2051.
13. W. Sheng, Q. Ye, W. Yu, R. Liu, M. Xu, J. Gao, Y. Jia, *Tetrahedron Letters* 2015, **56**, 599.
14. D. Rao, S. Rasheed, G. Raina, Q. Ahmed, C. Jaladanki, P. Bharatam, P. Das, *J. Org. Chem.* 2017, **82**, 7234.
15. B. Barron, W. Wong, P. Chiu, K. Hii, *ACS Catal.* **2016**, 6, 4189.
16. C. Whiteoak, O. Planas, A. Company, X. Ribasa, *Adv. Synth. Catal.* 2016, **358**, 1679.
17. X. Jia, P. Li, Yu Shao, Y. Yuan, H. Ji, W. Hou, X. Liu and X. Zhang, *Green Chem.*, 2017, **19**, 5568.

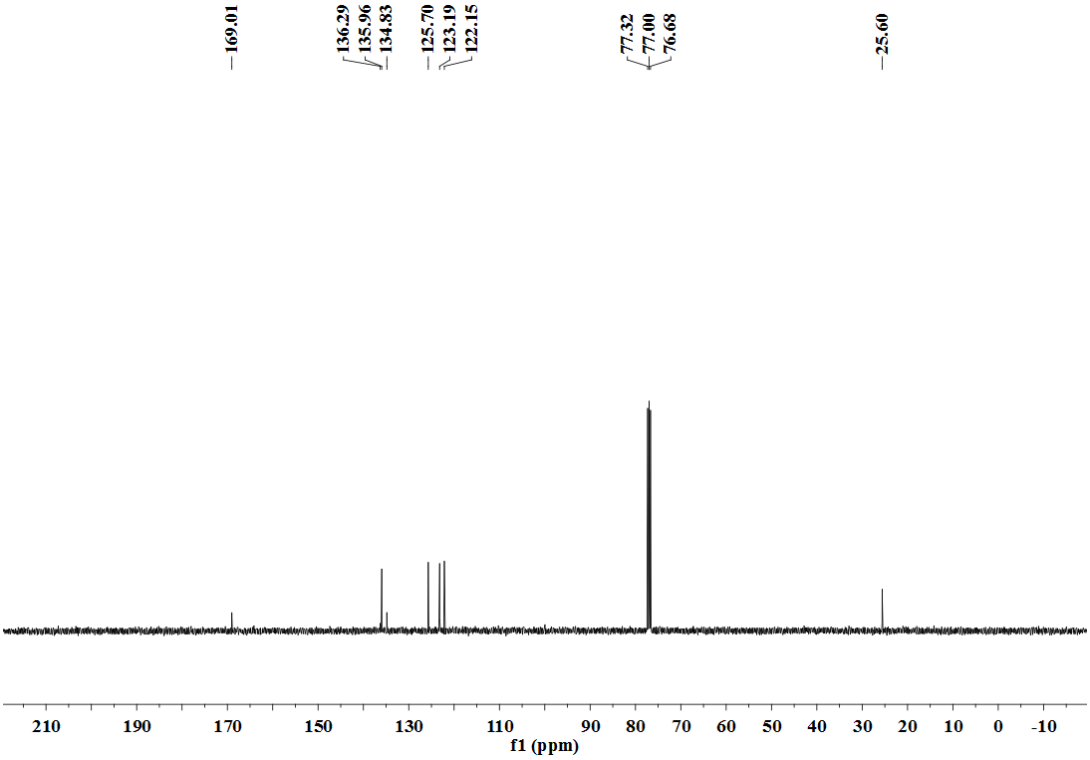
E. NMR Spectra

***N*-(2-Nitrophenyl)acetamide (2a)**

^{1}H NMR

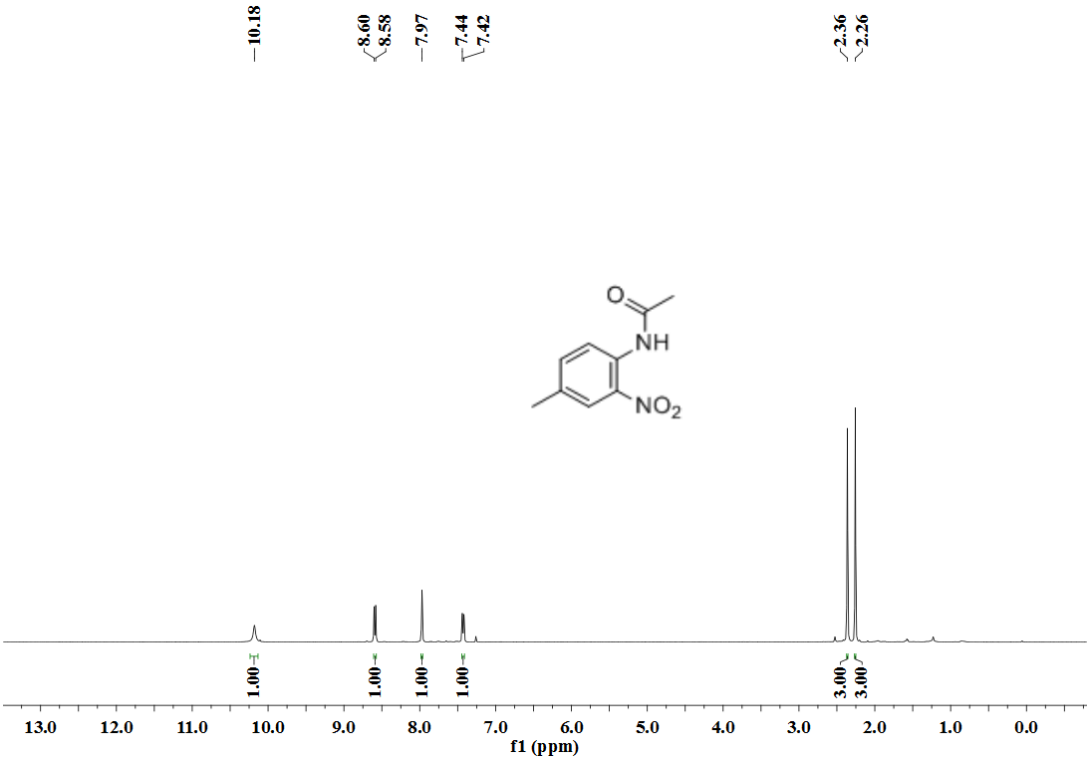


^{13}C NMR

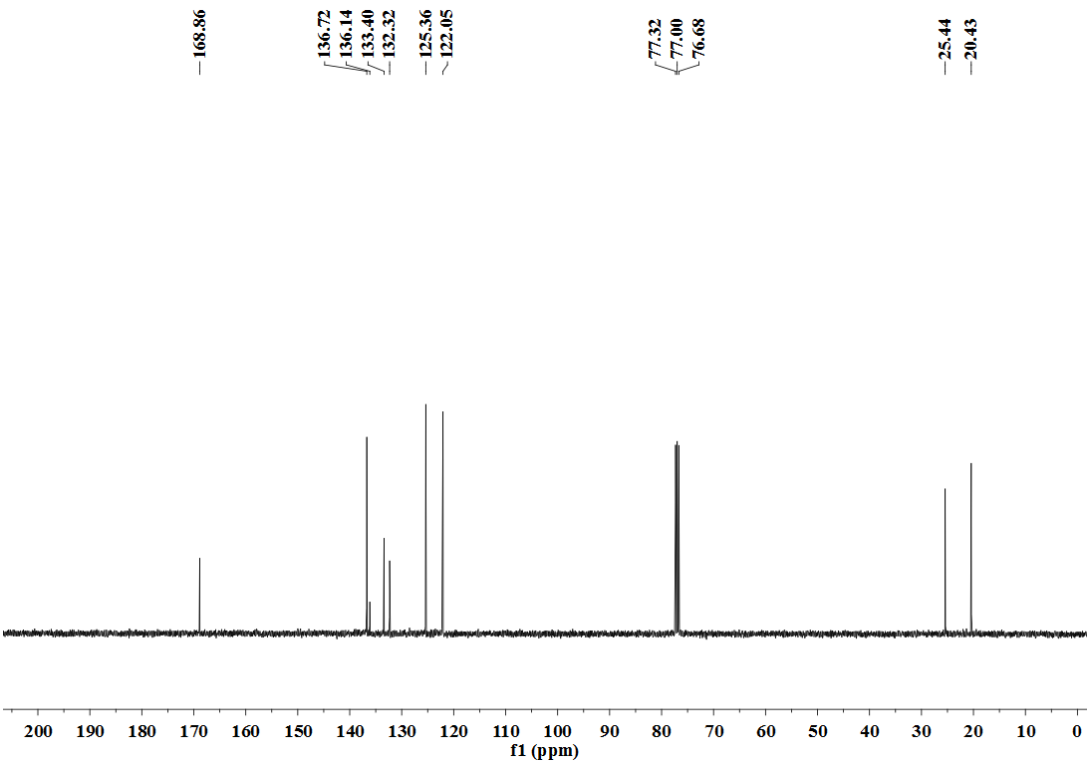


***N*-(4-Methyl-2-nitrophenyl)acetamide (2b)**

^{1}H NMR

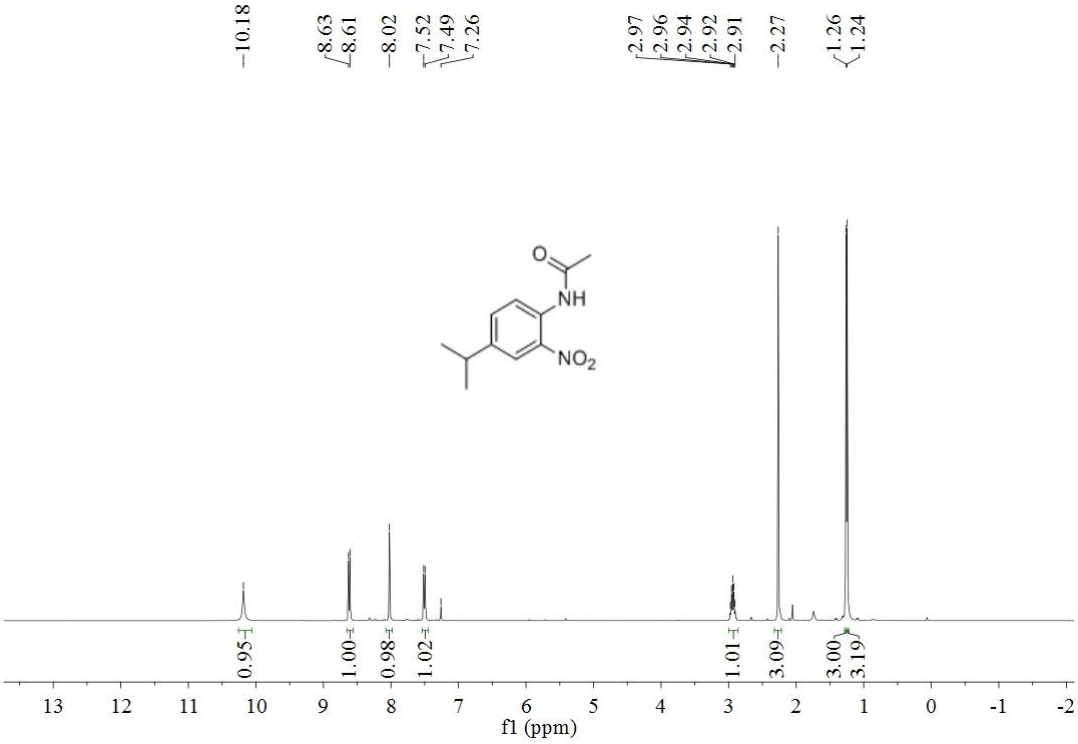


^{13}C NMR

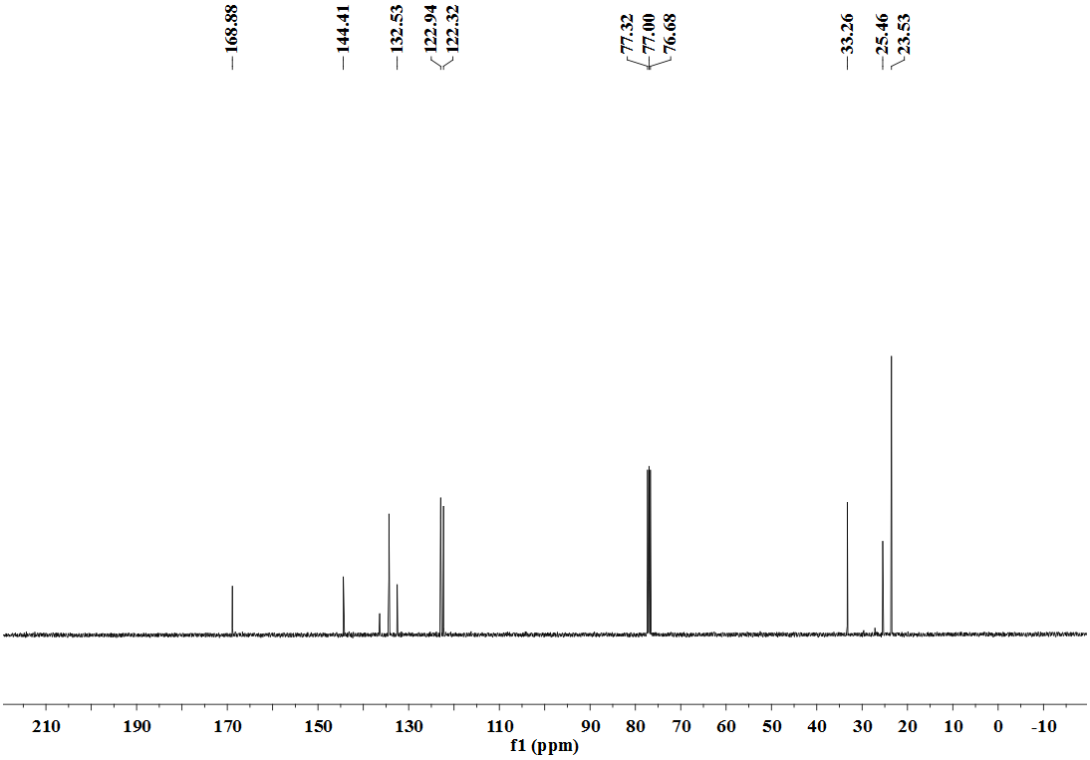


***N*-(4-*iso*-Propyl-2-nitrophenyl)acetamide (2c)**

^{1}H NMR

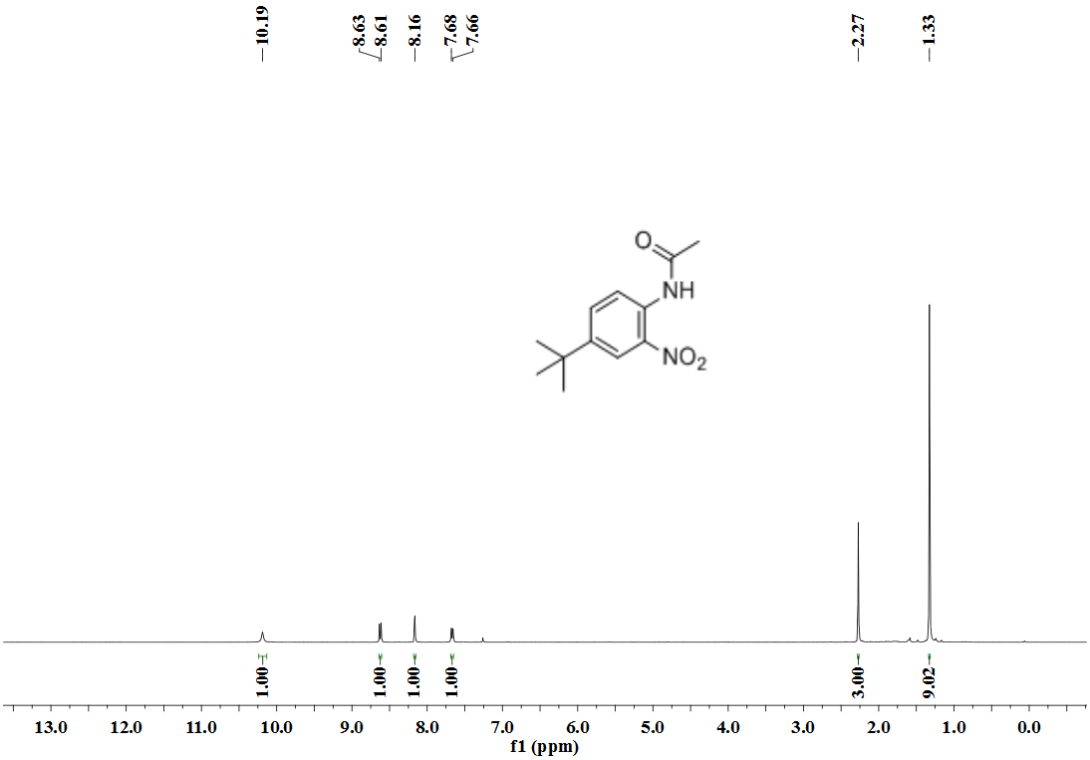


^{13}C NMR

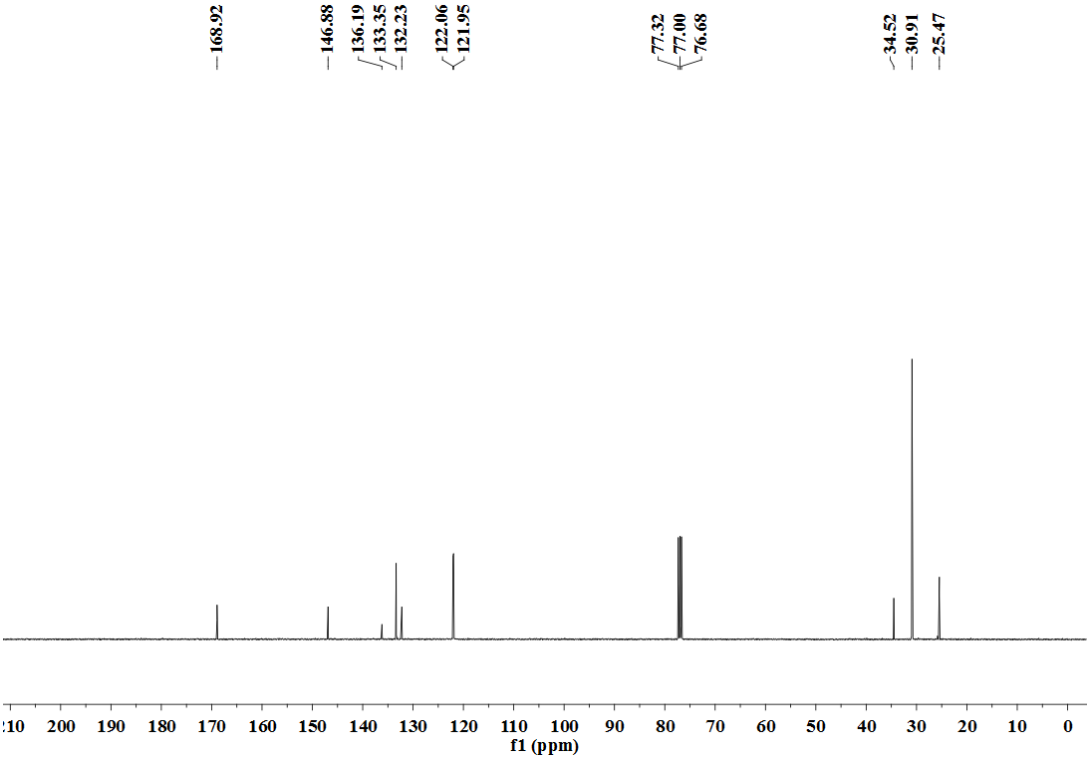


N-(4-(*tert*-Butyl)-2-nitrophenyl)acetamide (2d)

^{1}H NMR

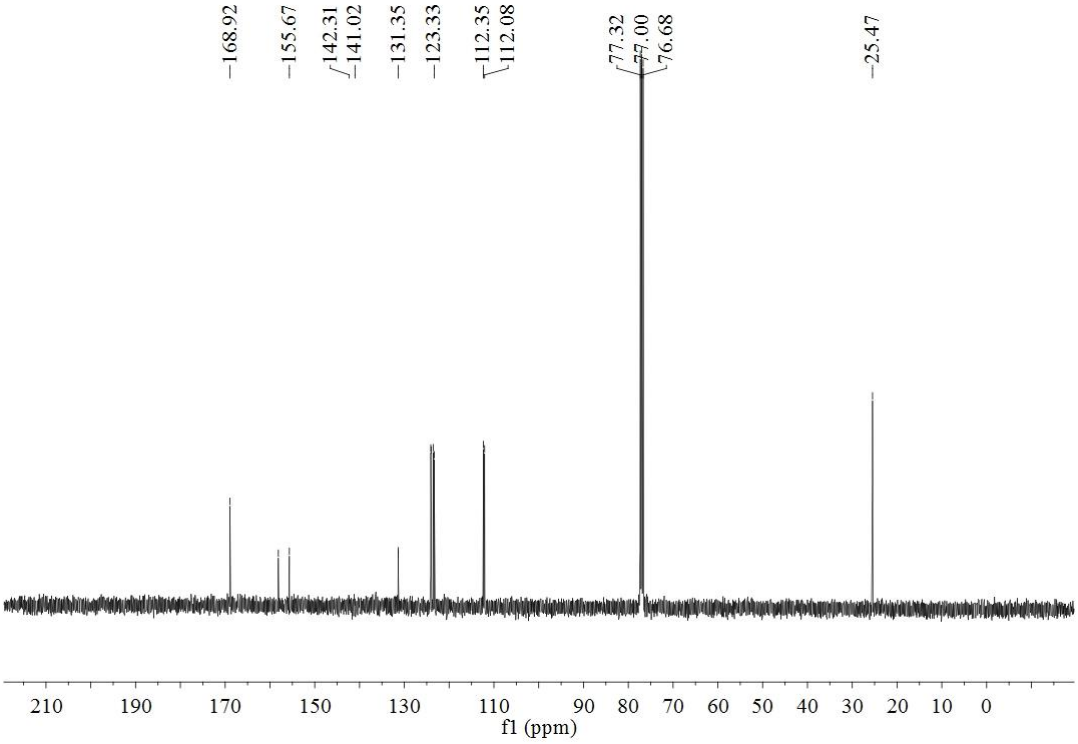


^{13}C NMR

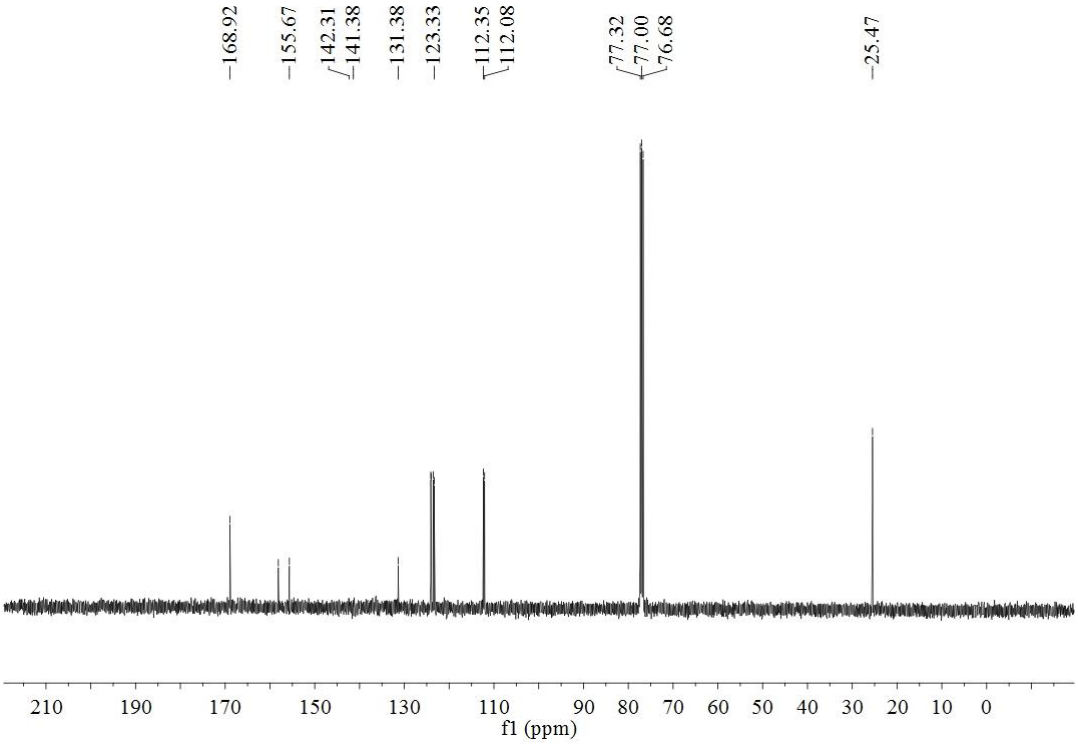


***N*-(4-Fluoro-2-nitrophenyl)acetamide (2e)**

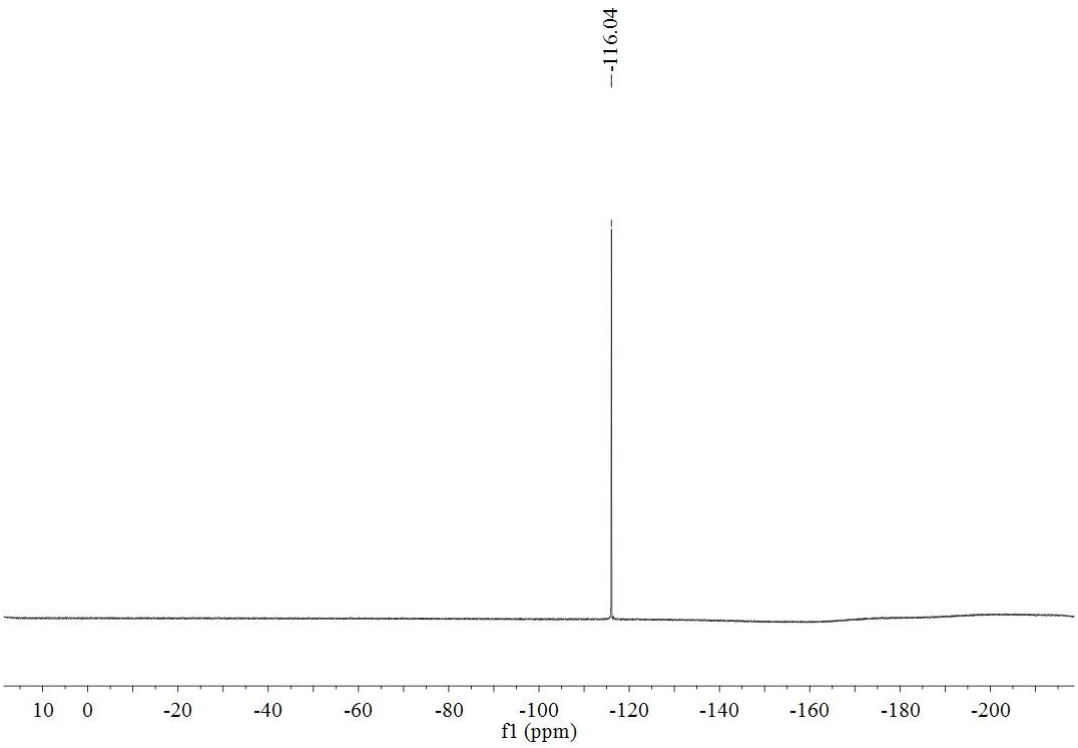
^{1}H NMR



^{13}C NMR

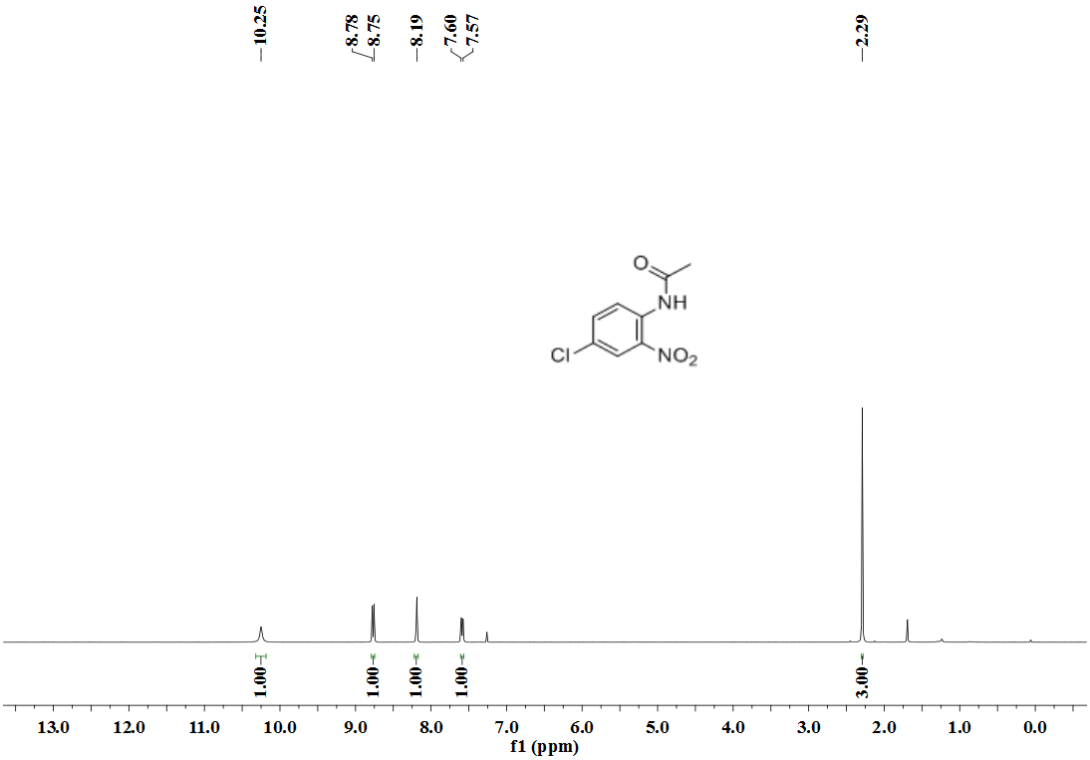


^{19}F NMR

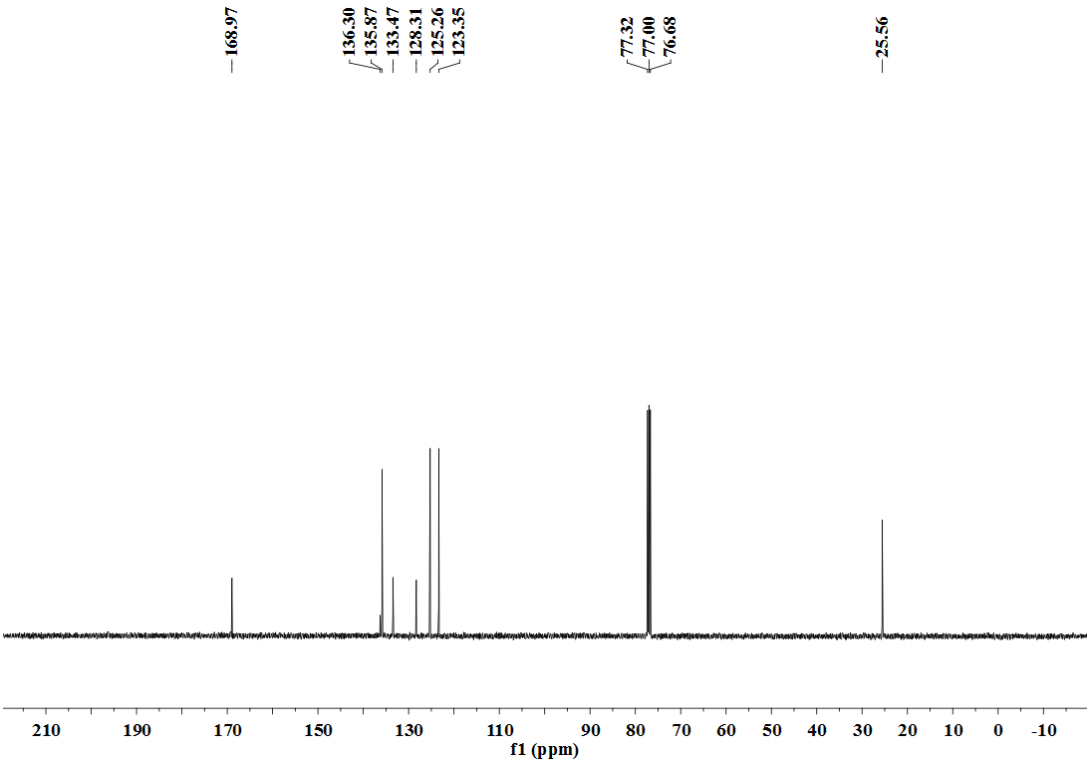

-116.04
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

***N*-(4-Chloro-2-nitrophenyl)acetamide (2f)**

^{1}H NMR

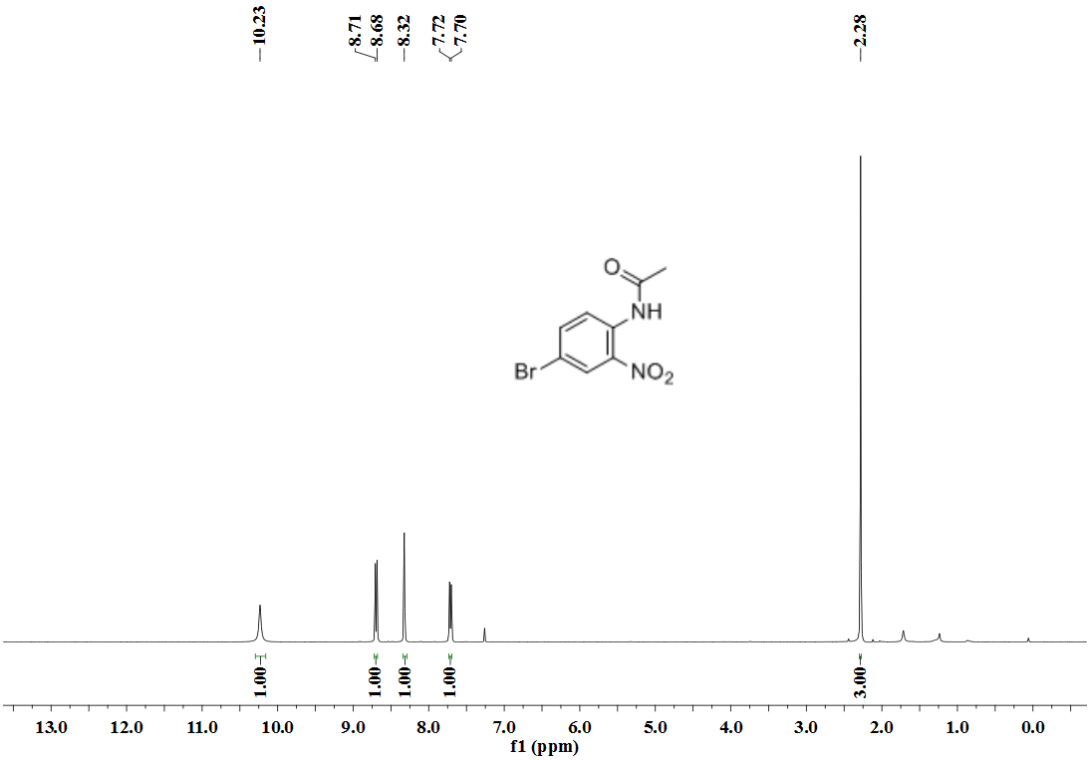


^{13}C NMR

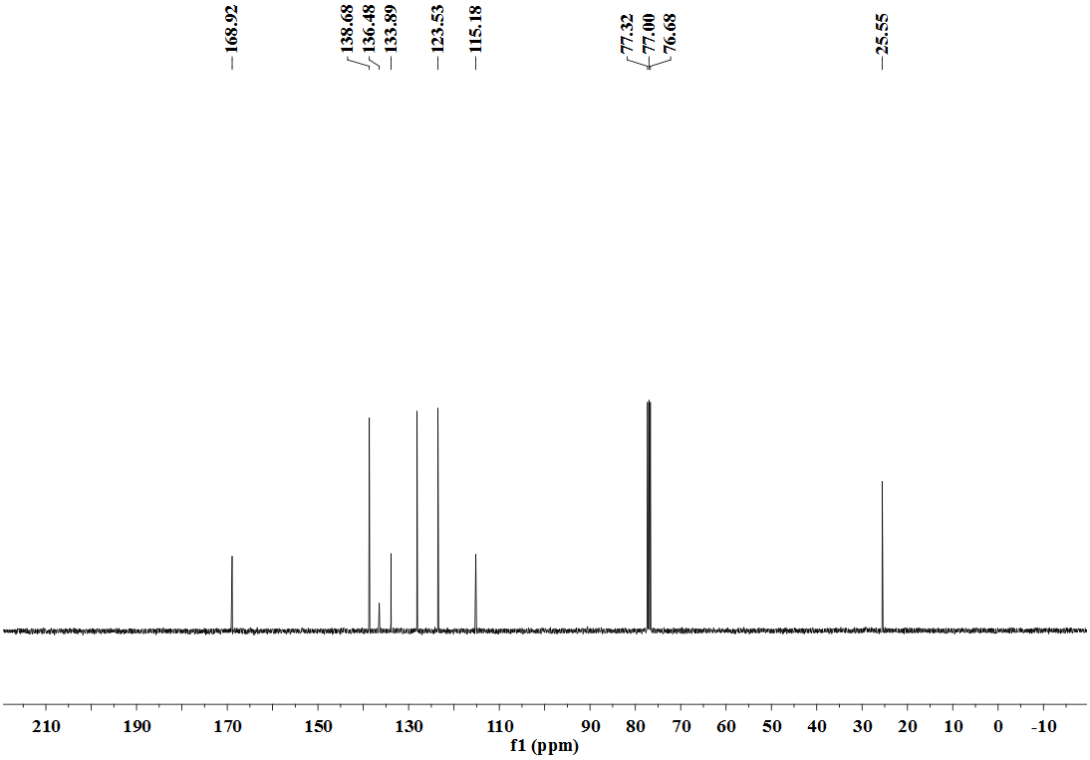


***N*-(4-Bromo-2-nitrophenyl)acetamide (2g)**

^{1}H NMR

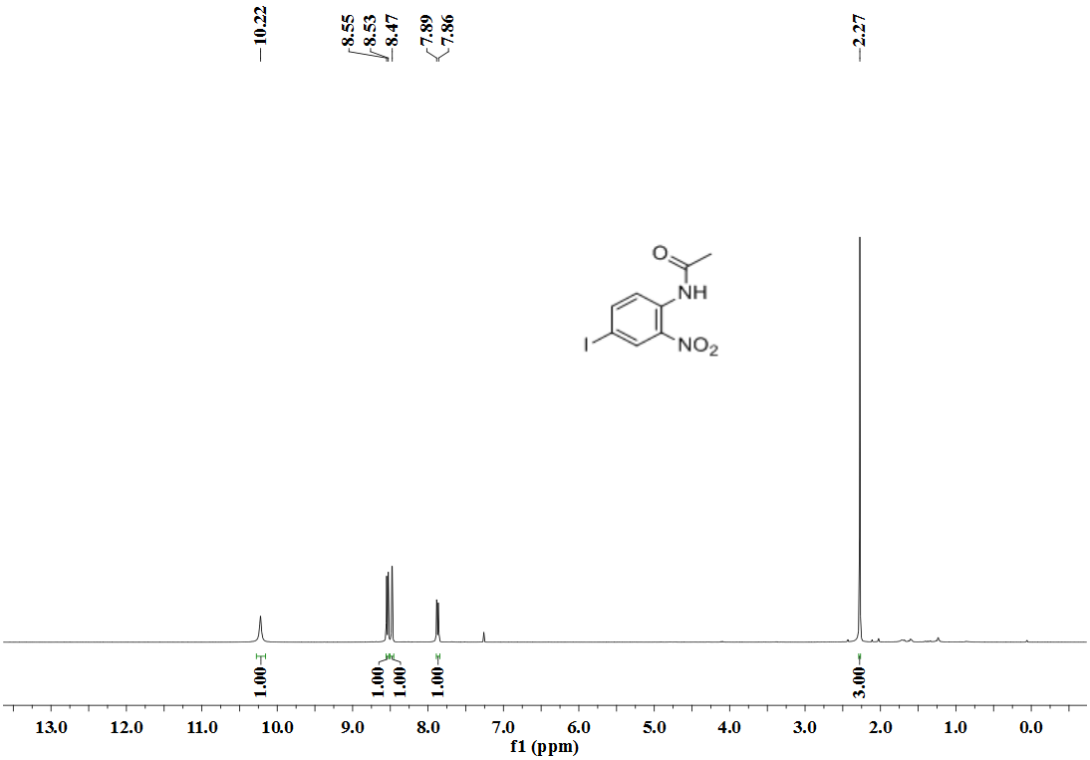


^{13}C NMR

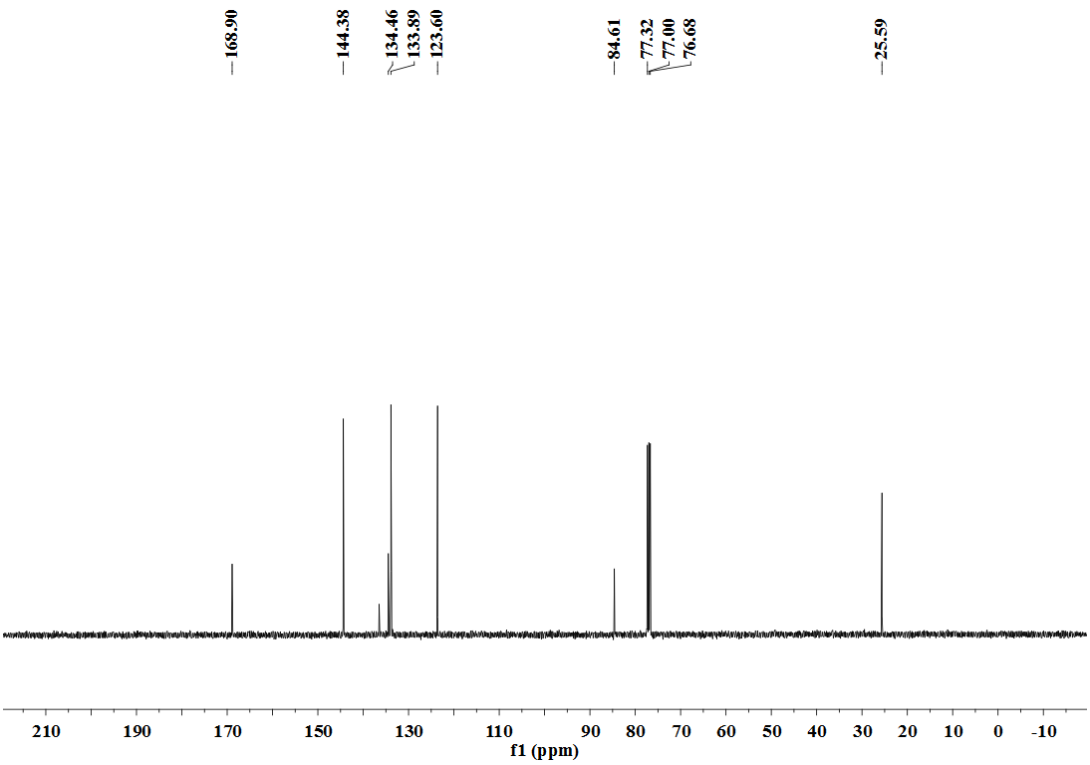


***N*-(4-Iodo-2-nitrophenyl)acetamide (2h)**

^{1}H NMR

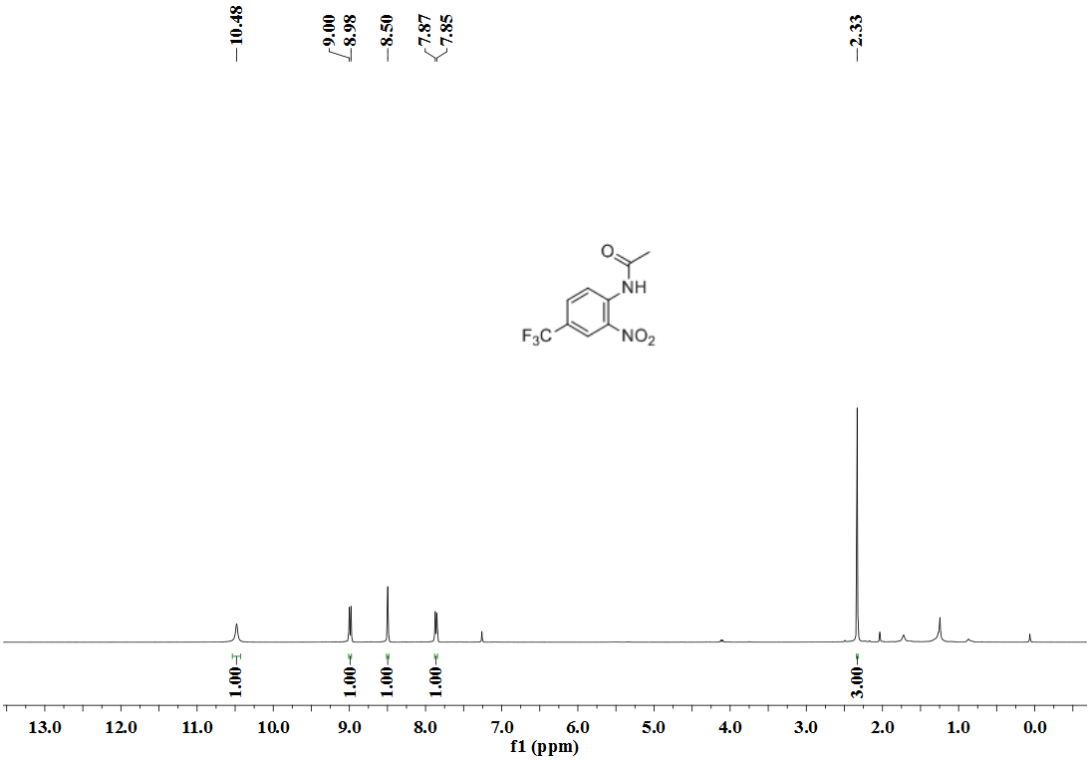


^{13}C NMR

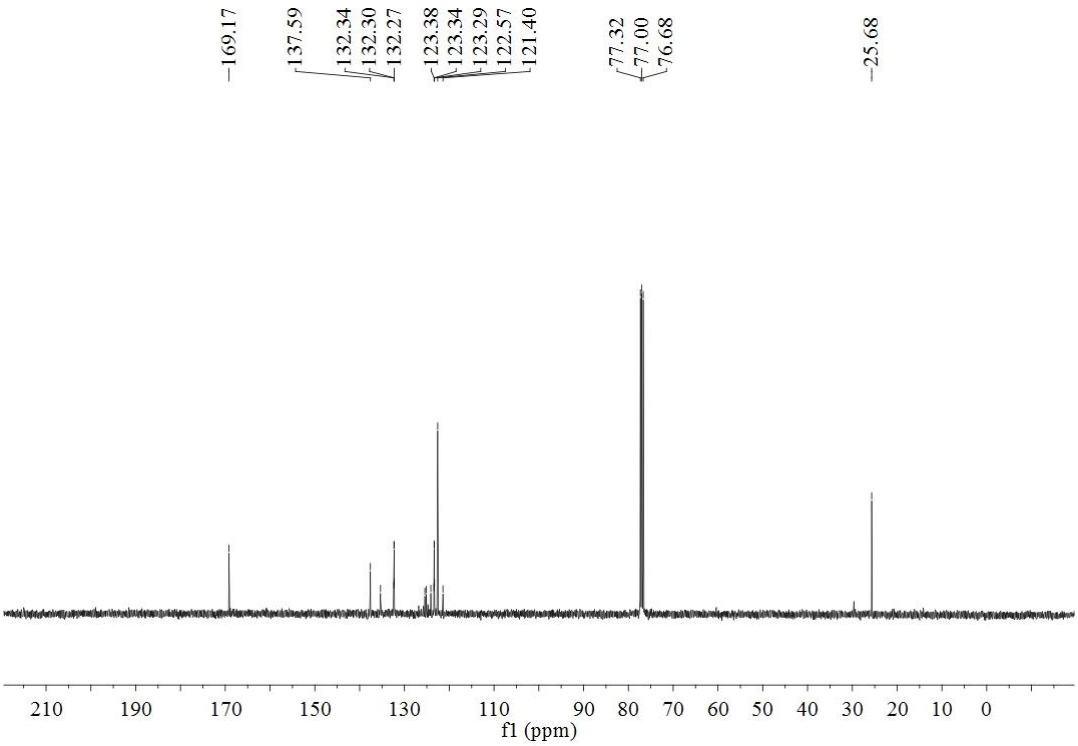


***N*-(2-Nitro-4-(trifluoromethyl)phenyl)acetamide (2i)**

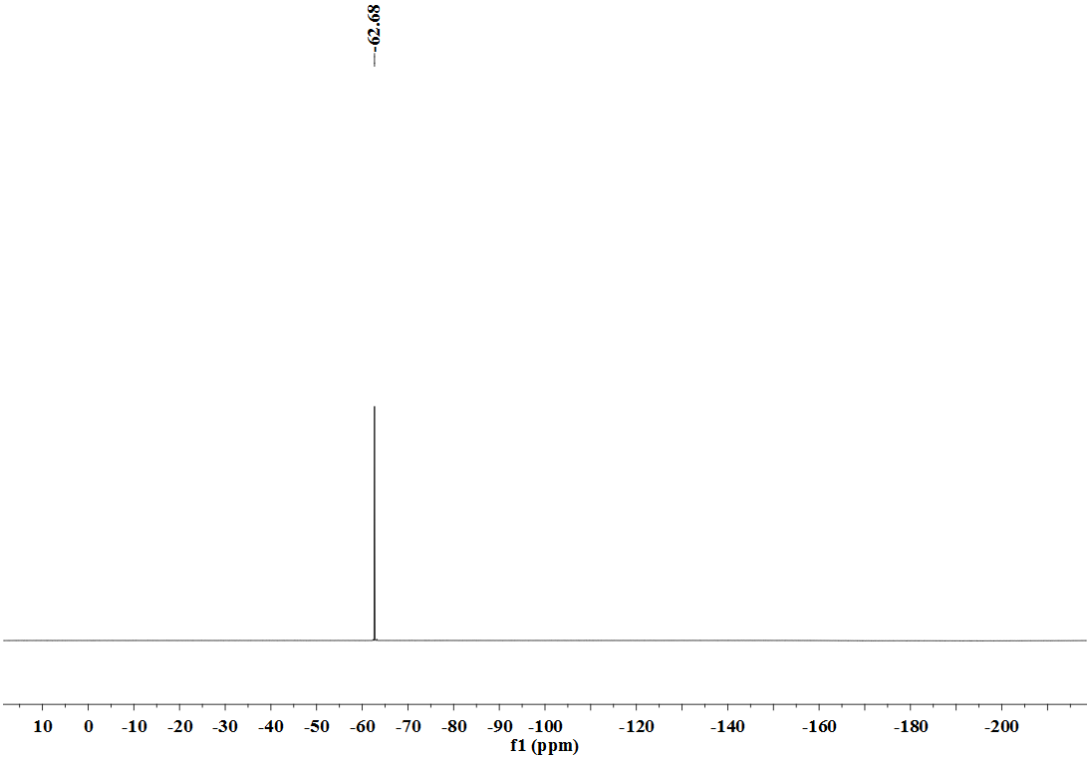
^{1}H NMR



^{13}C NMR

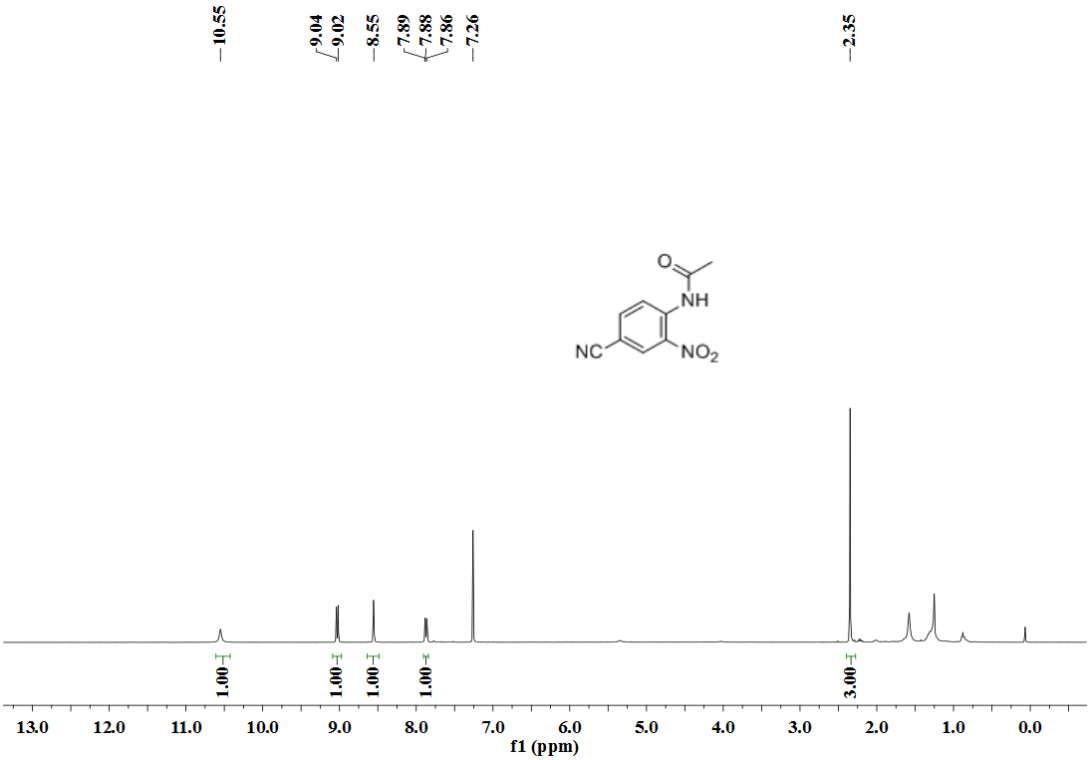


^{19}F NMR

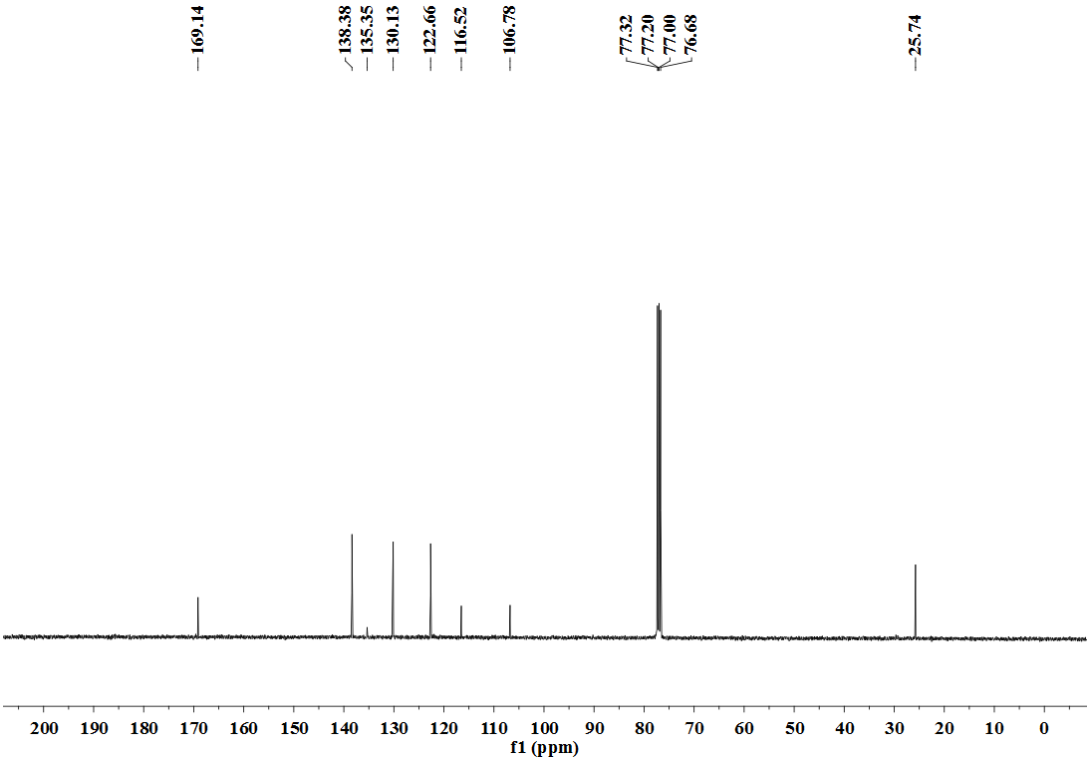

-62.68
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

N-(4-Cyano-2-nitrophenyl)acetamide (2j)

^{1}H NMR

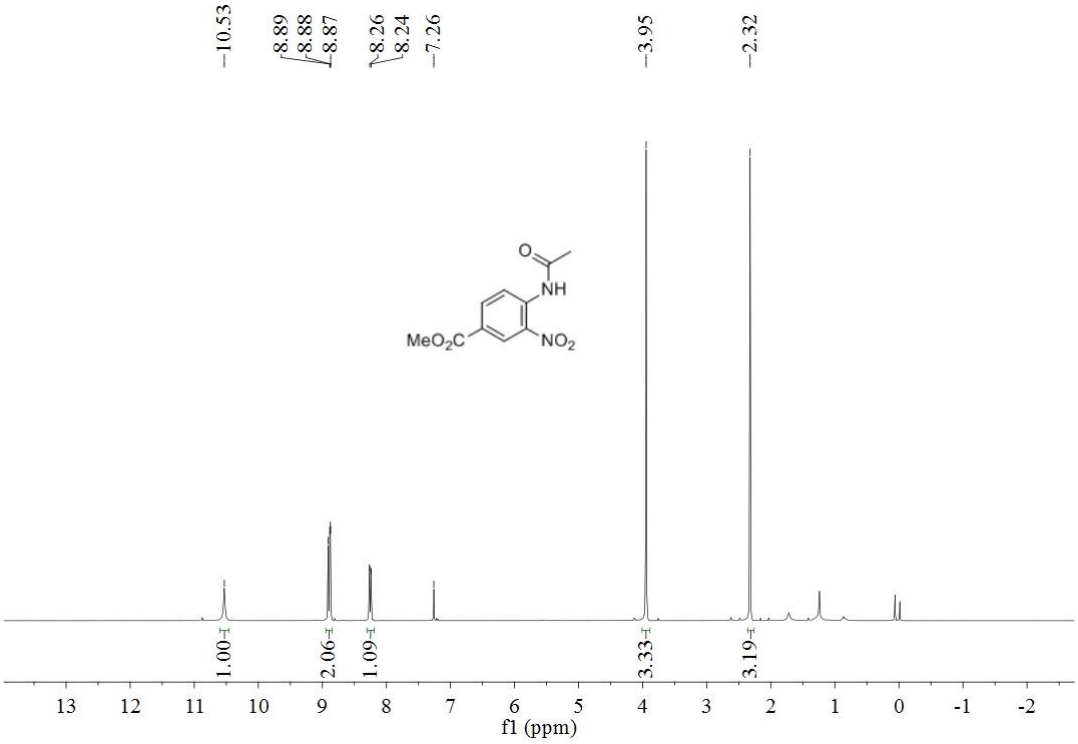


^{13}C NMR

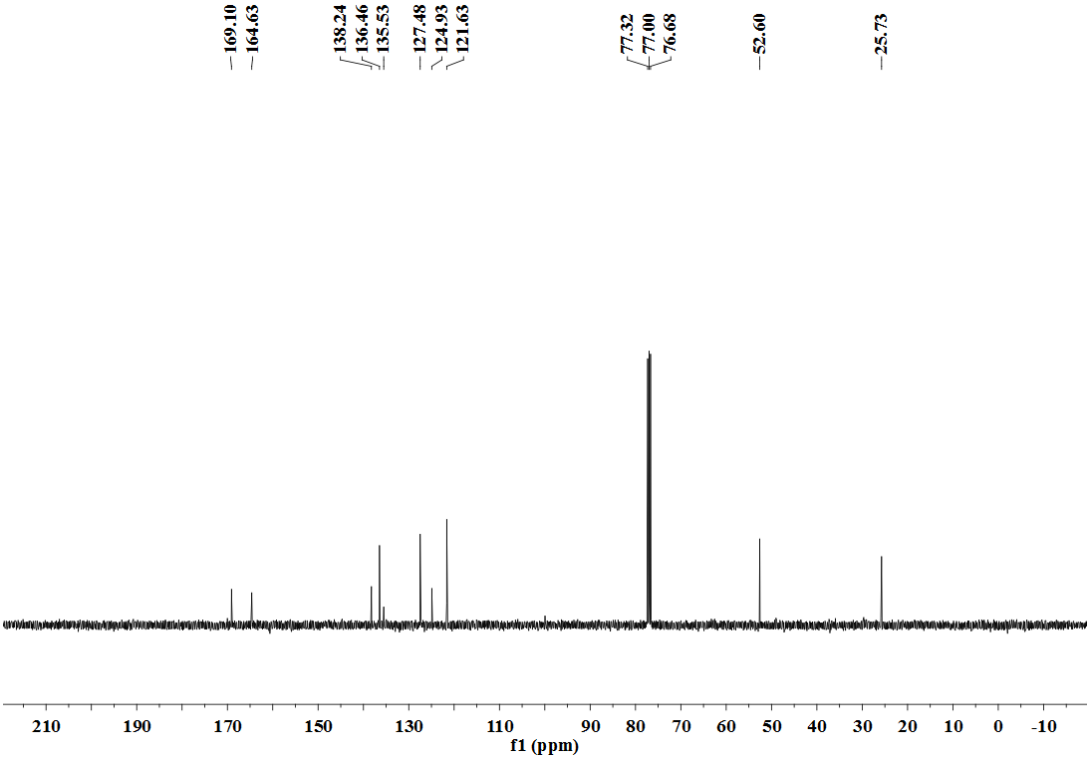


Methyl 4-acetamido-3-nitrobenzoate (2k)

^{1}H NMR

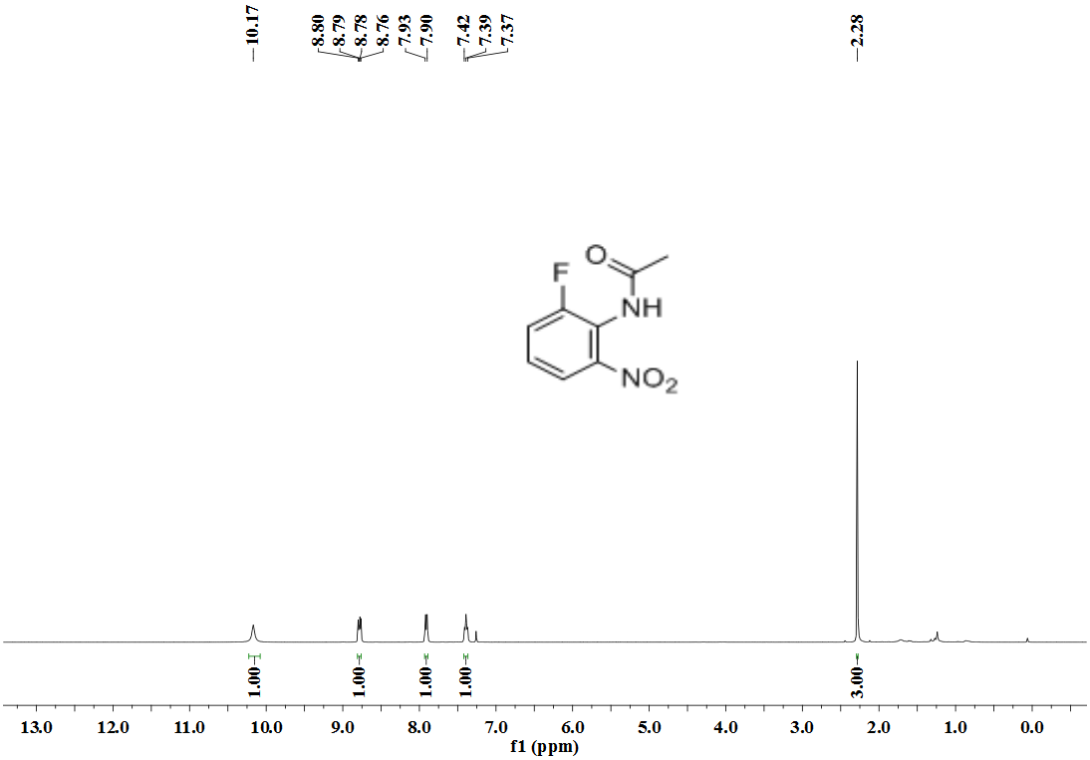


^{13}C NMR

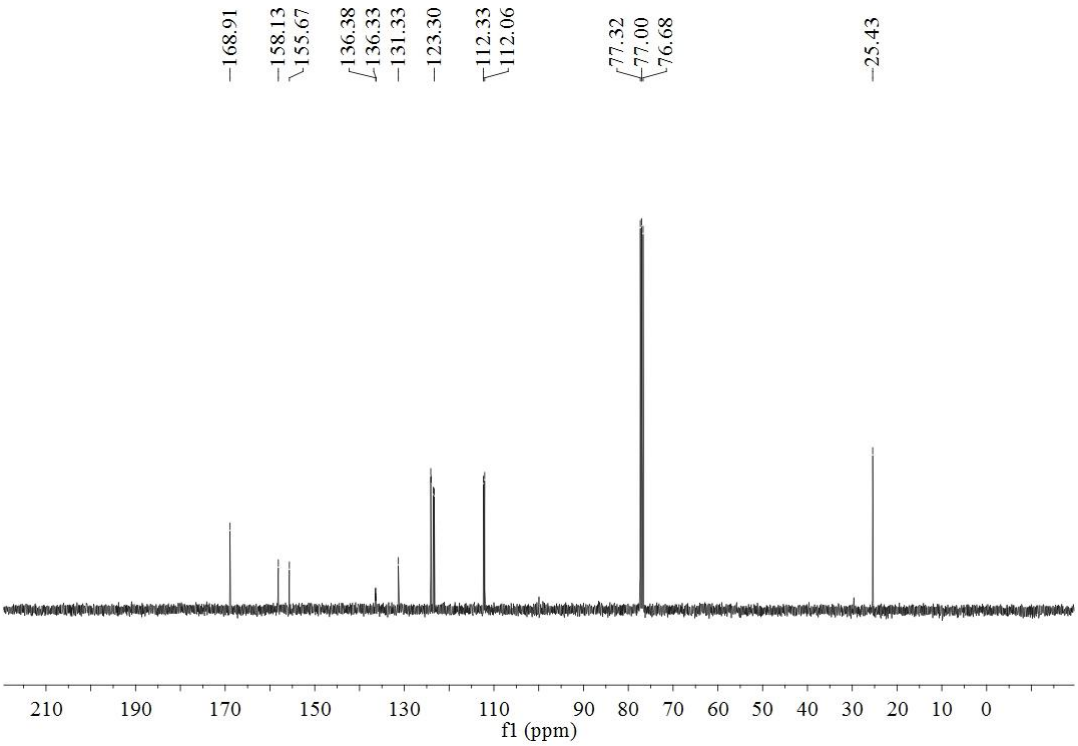


***N*-(2-Fluoro-6-nitrophenyl)acetamide (2l)**

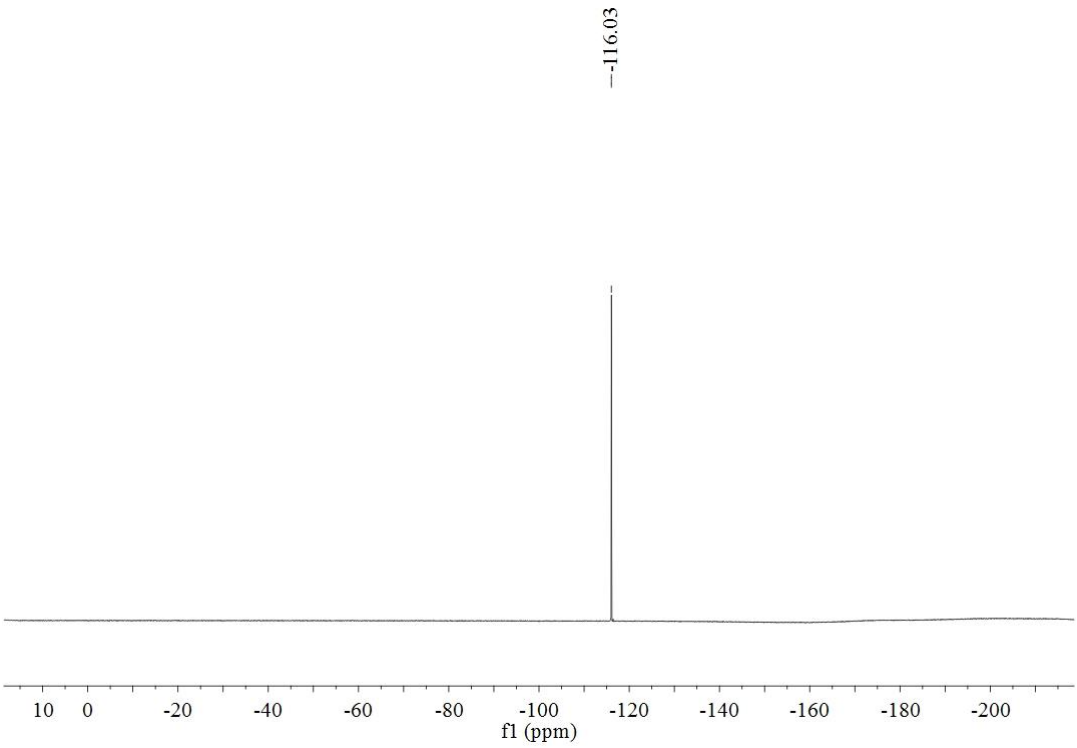
^{1}H NMR



^{13}C NMR

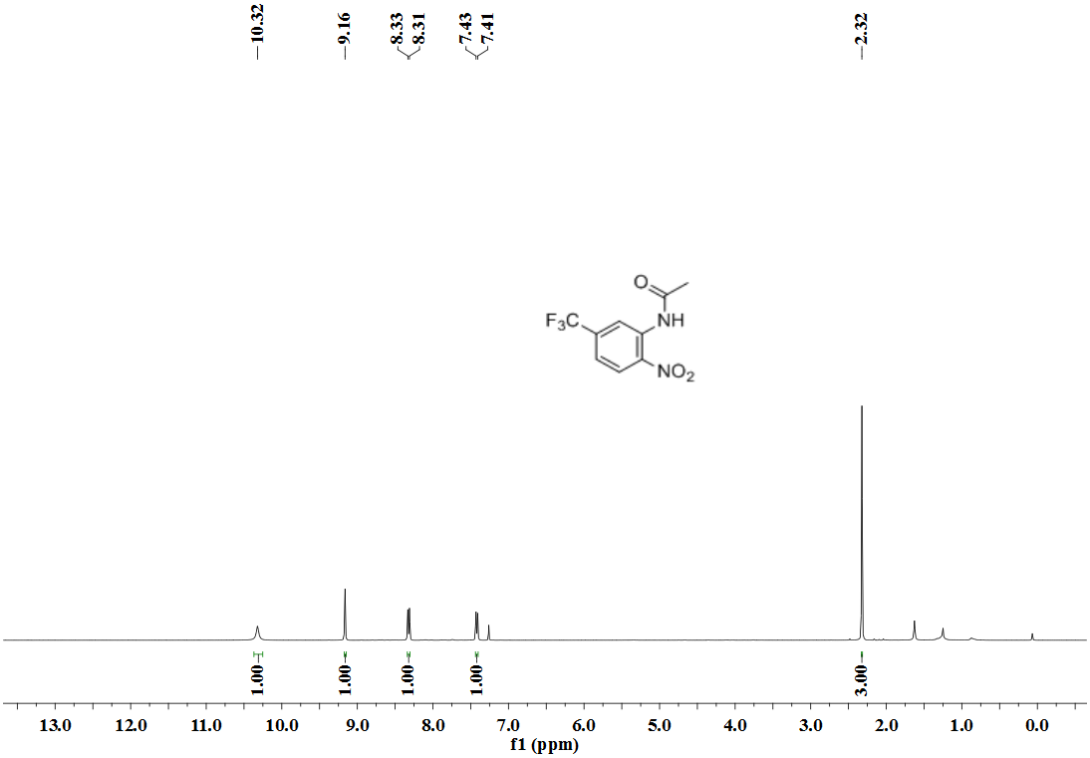


^{19}F NMR

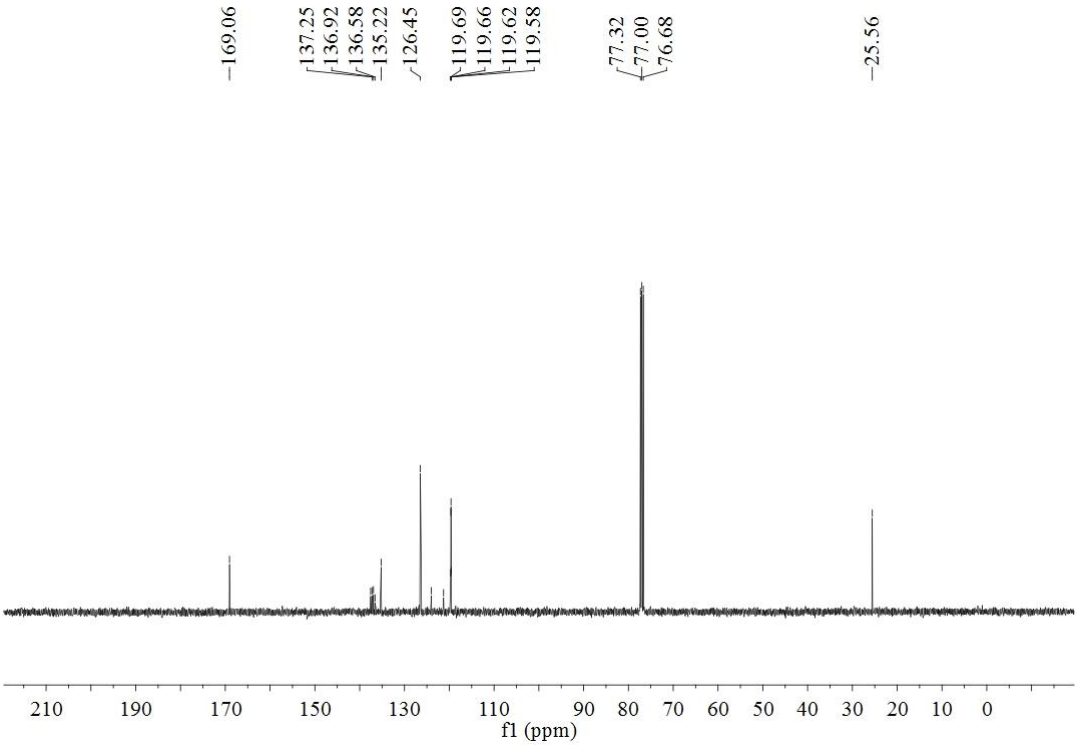

-116.03
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

***N*-(2-Nitro-5-(trifluoromethyl)phenyl)acetamide (2m)**

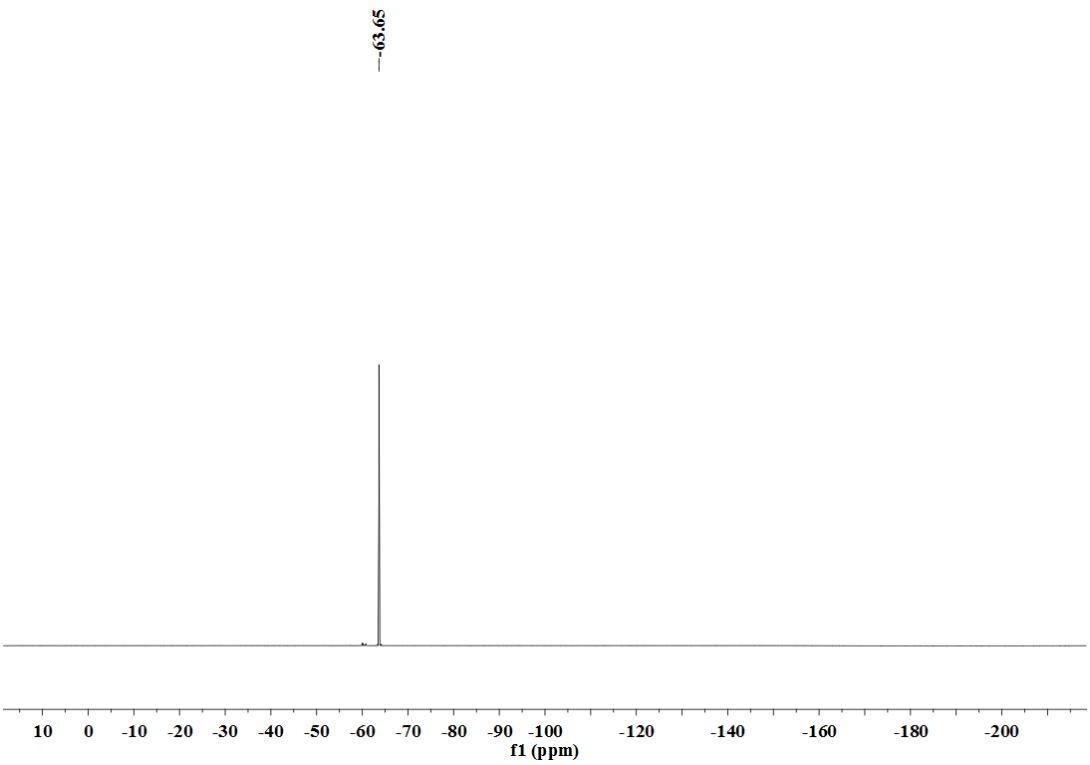
^{1}H NMR



^{13}C NMR

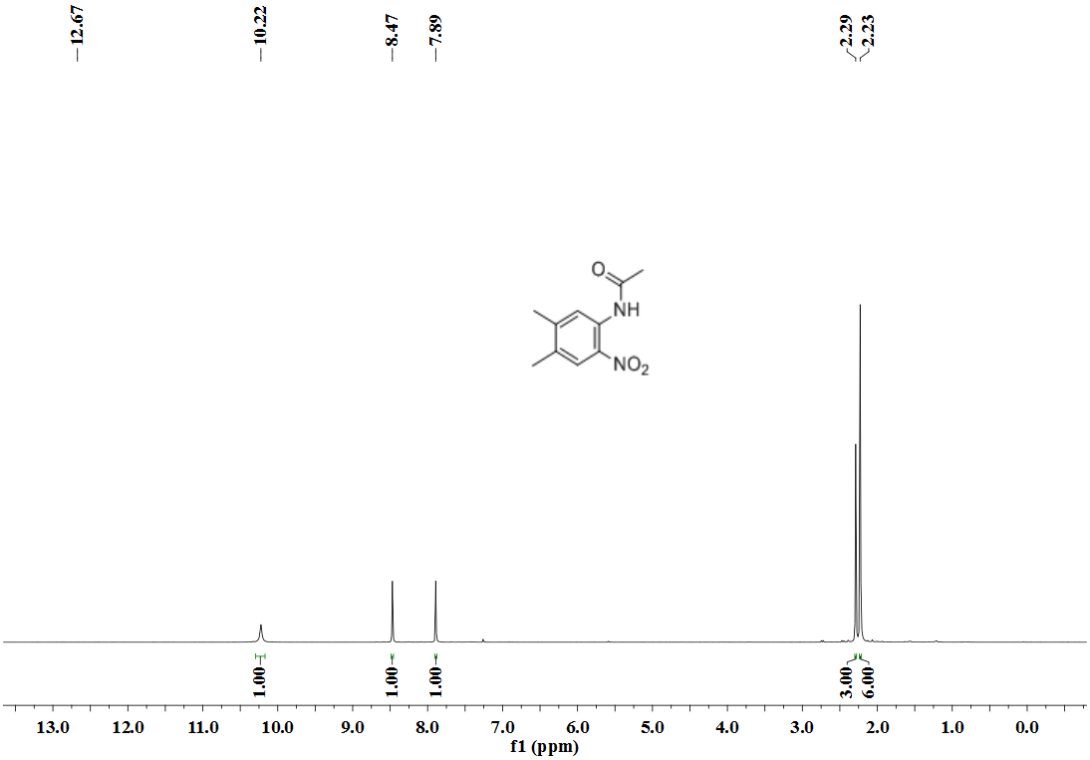


^{19}F NMR

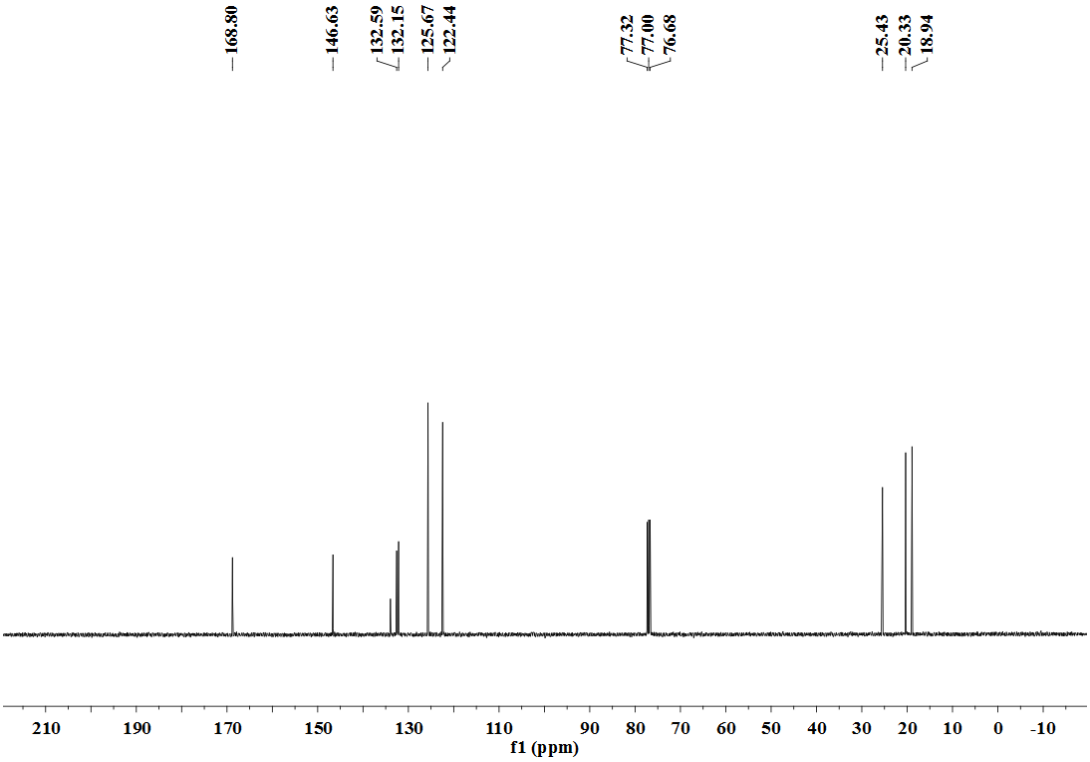

-63.65
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

_N_-(4,5-Dimethyl-2-nitrophenyl)acetamide (2n)

^{1}H NMR

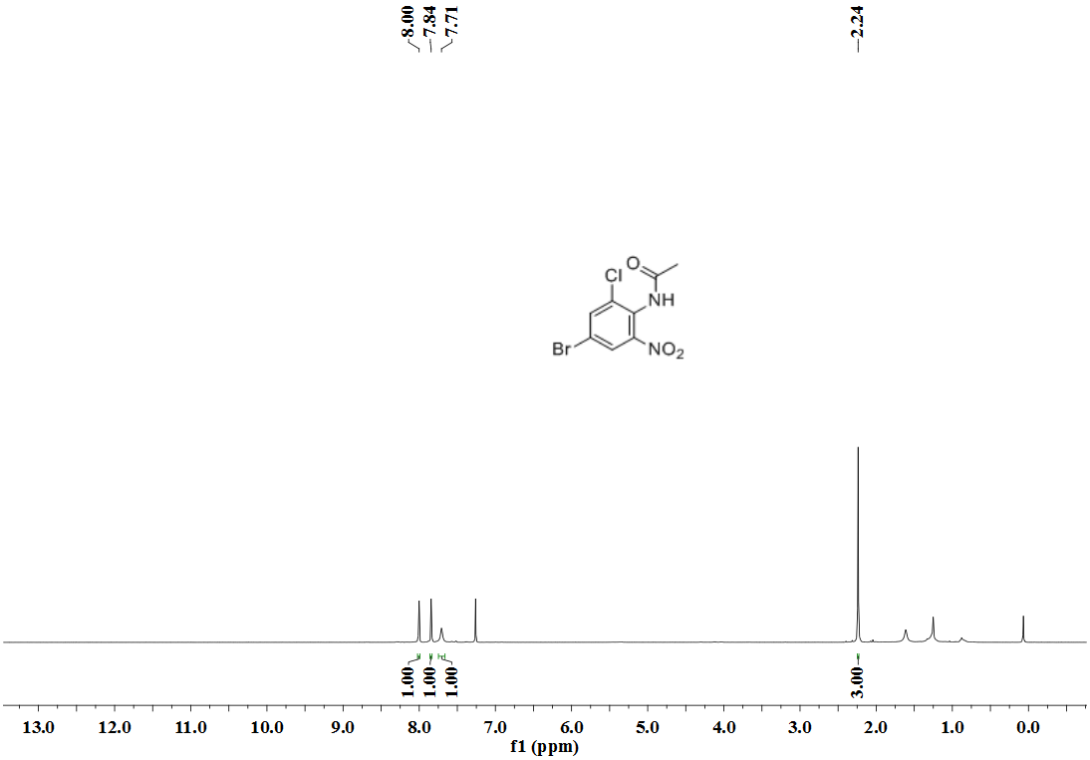


^{13}C NMR

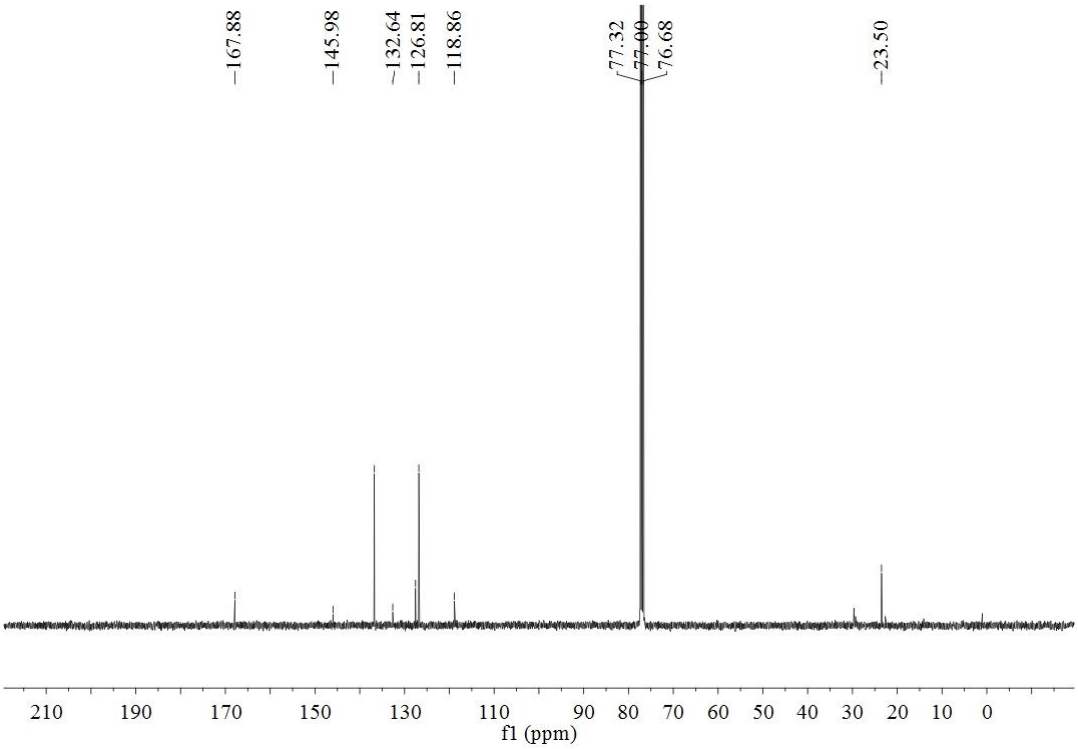


***N*-(4-Bromo-2-chloro-6-nitrophenyl)acetamide (2o)**

^{1}H NMR

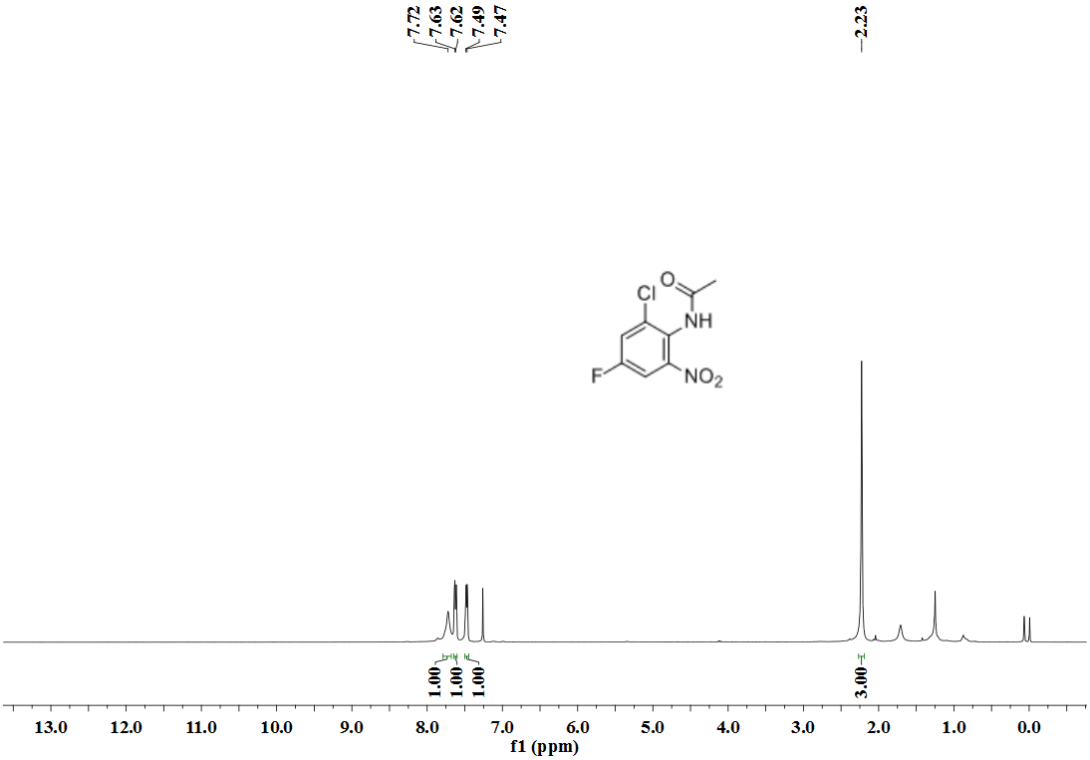


^{13}C NMR

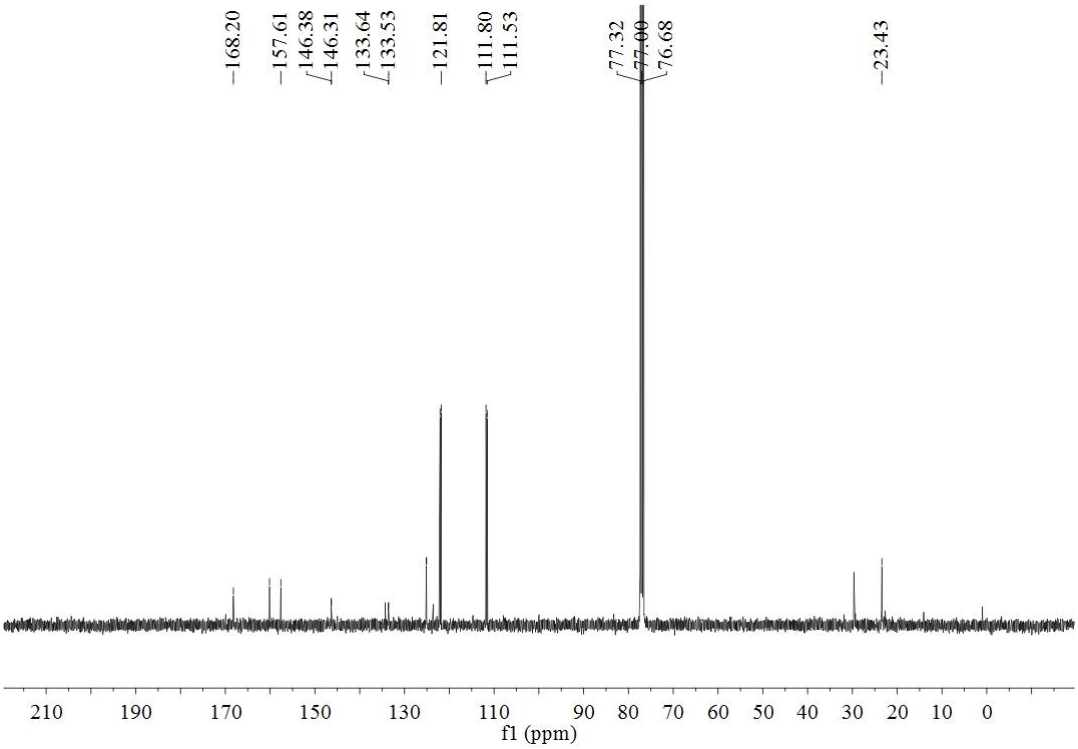


***N*-(2-Chloro-4-fluoro-6-nitrophenyl)acetamide (2p)**

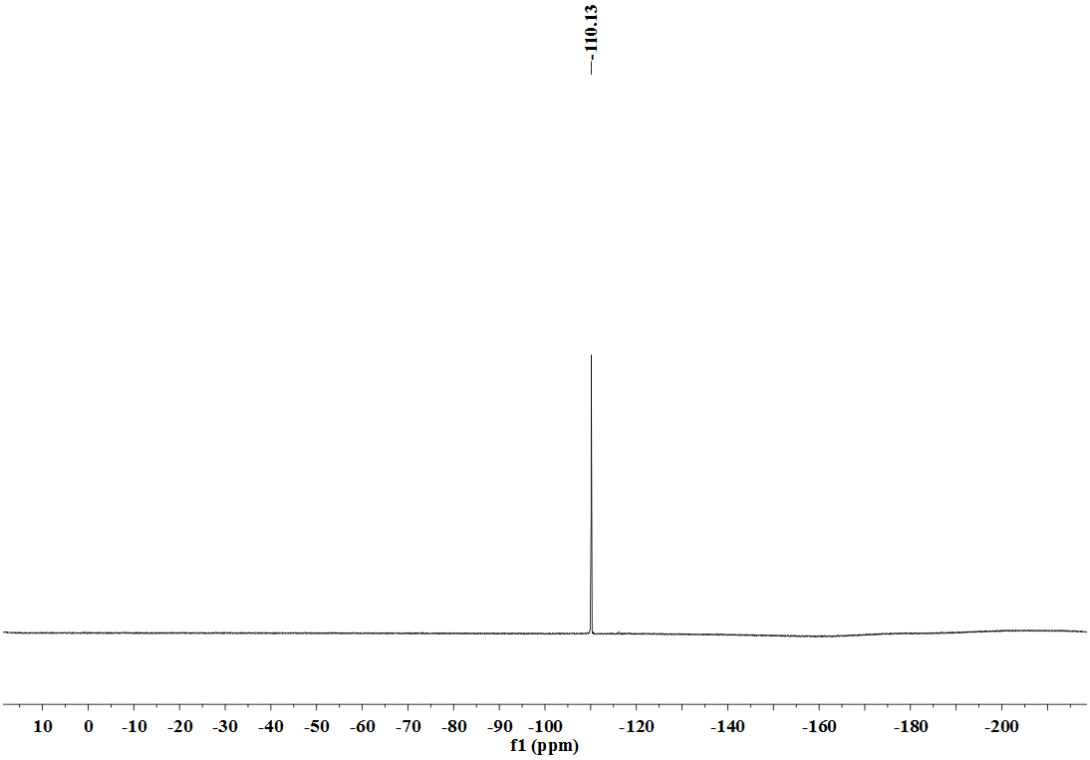
^{1}H NMR



^{13}C NMR

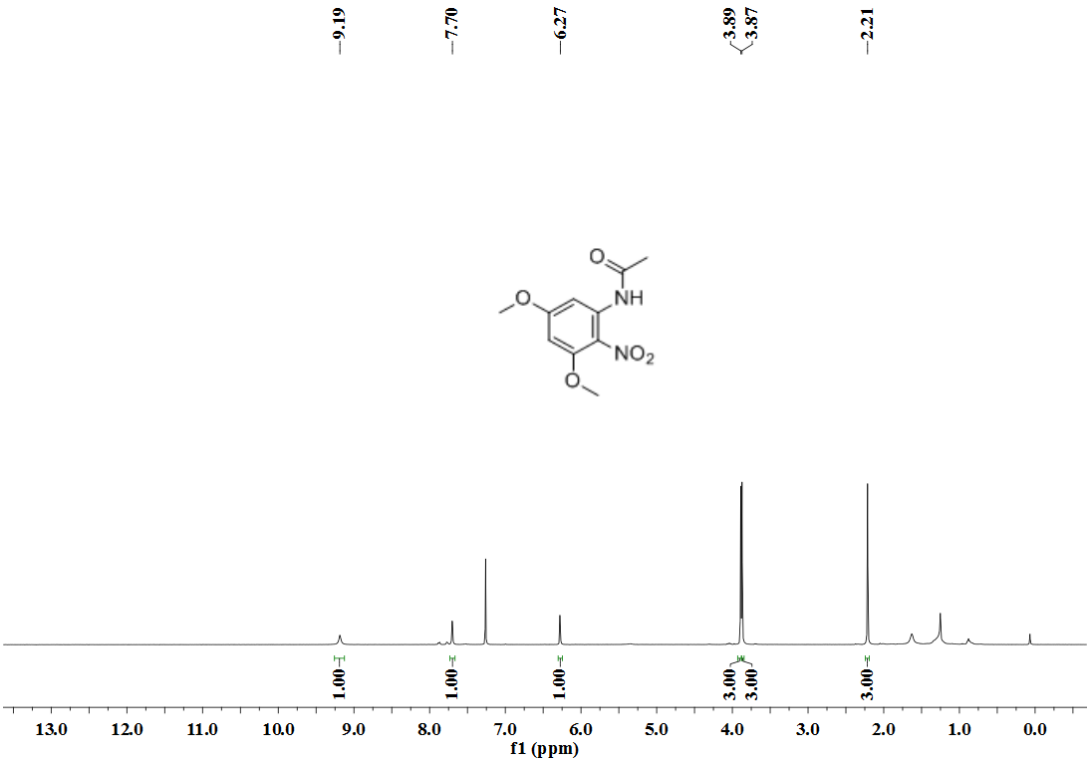


^{19}F NMR

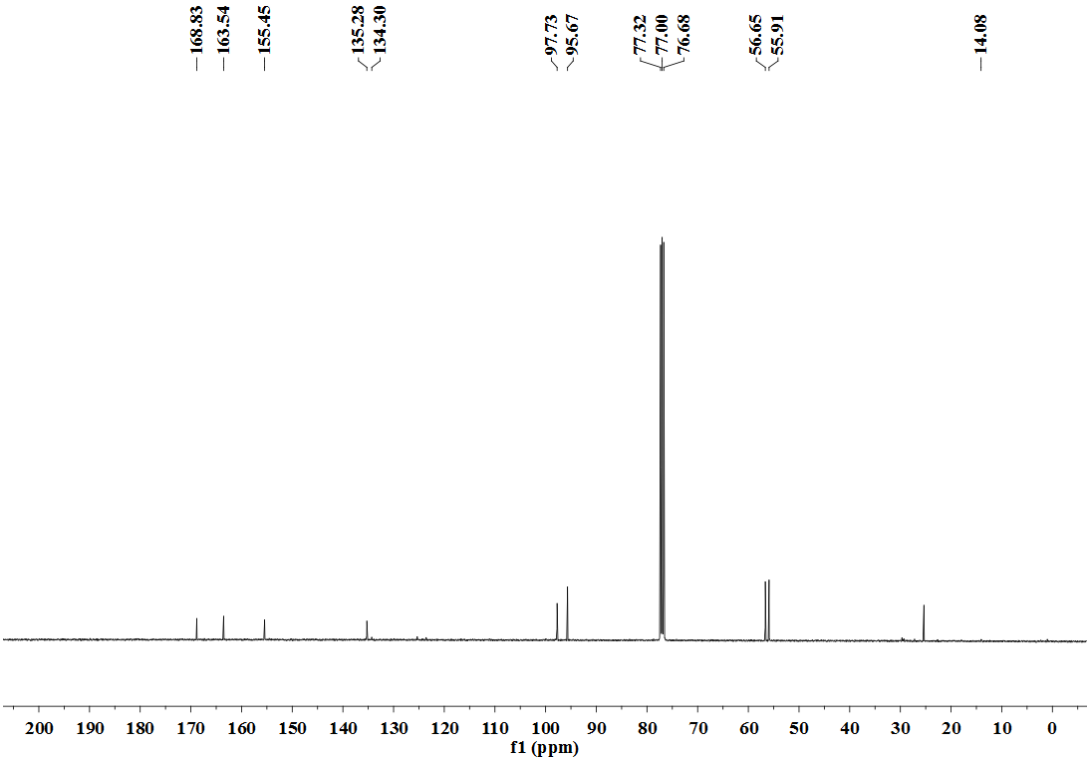


***N*-(3,5-Dimethoxy-2-nitrophenyl)acetamide (2q)**

^{1}H NMR

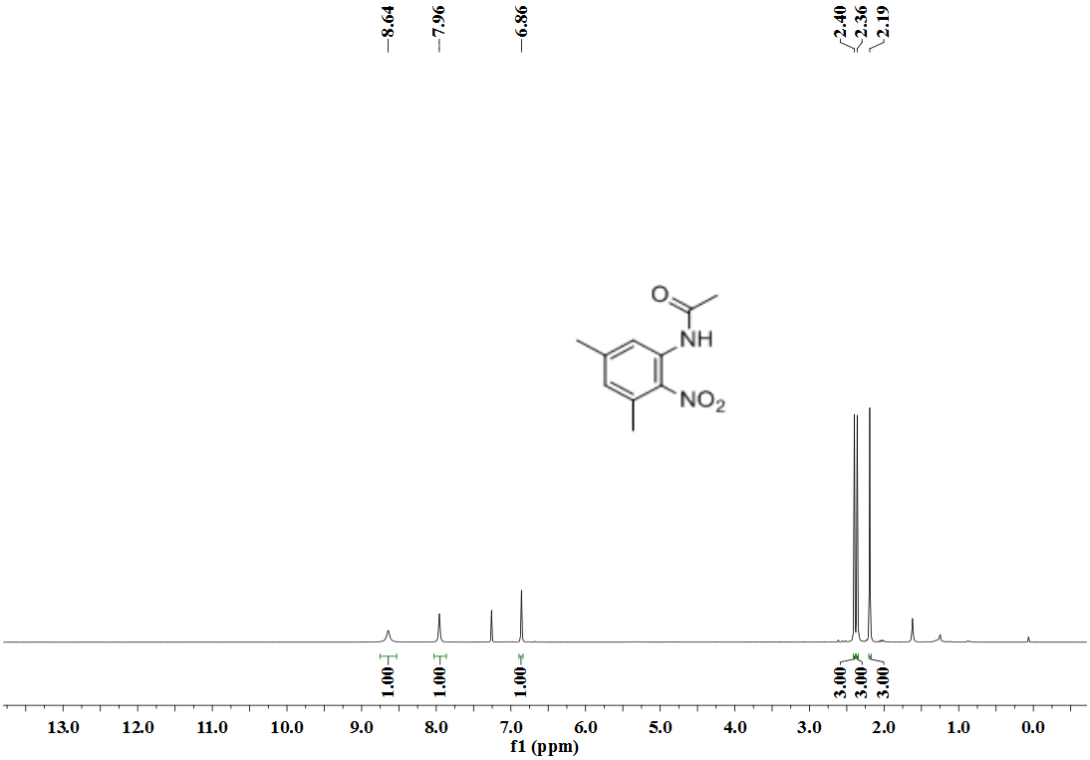


^{13}C NMR

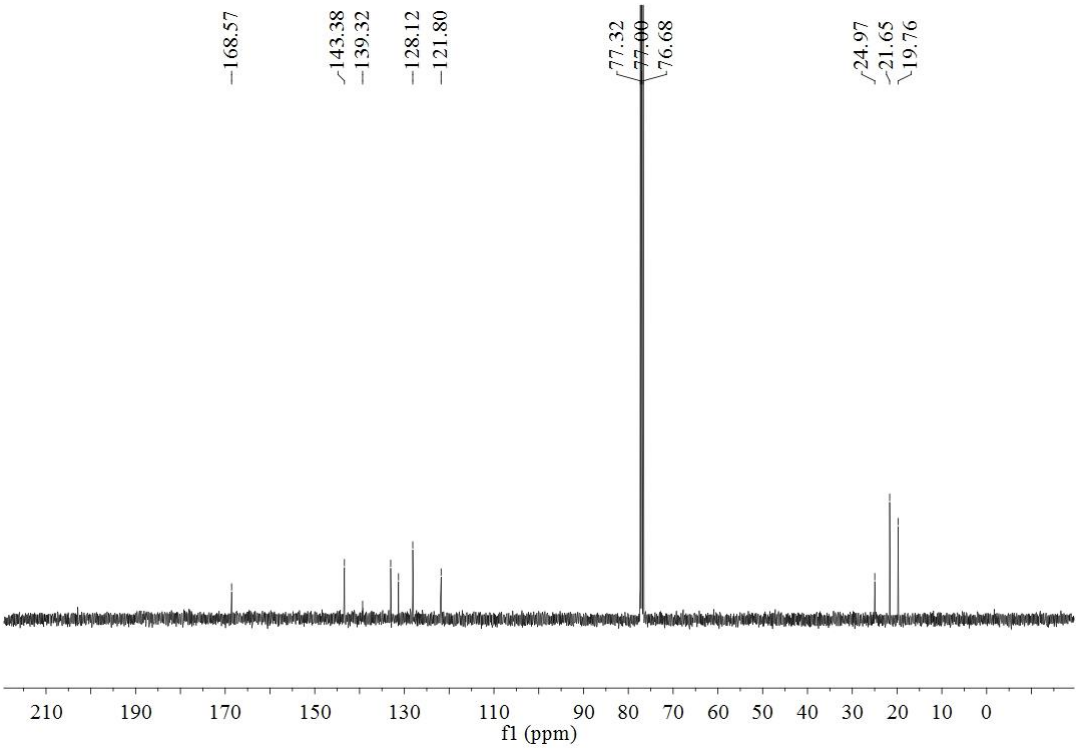


***N*-(3,5-Dimethyl-2-nitrophenyl)acetamide (2r)**

^{1}H NMR

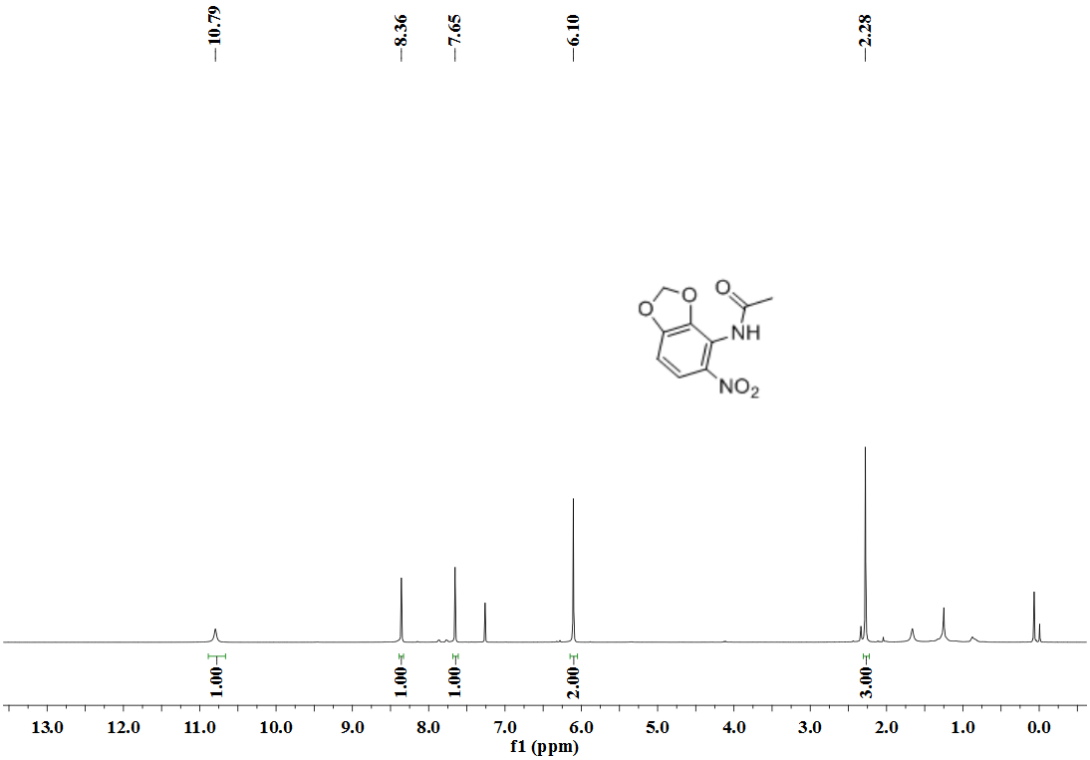


^{13}C NMR

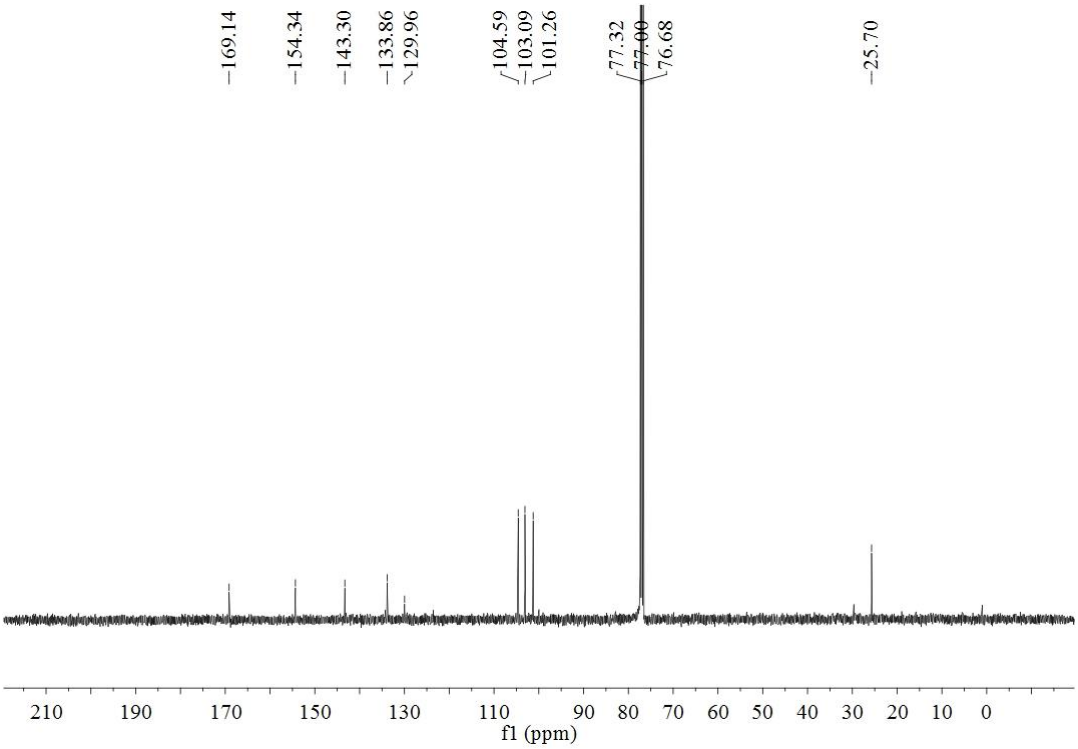


***N*-(5-Nitrobenzo[*d*][1,3]dioxol-4-yl)acetamide (2s)**

^{1}H NMR

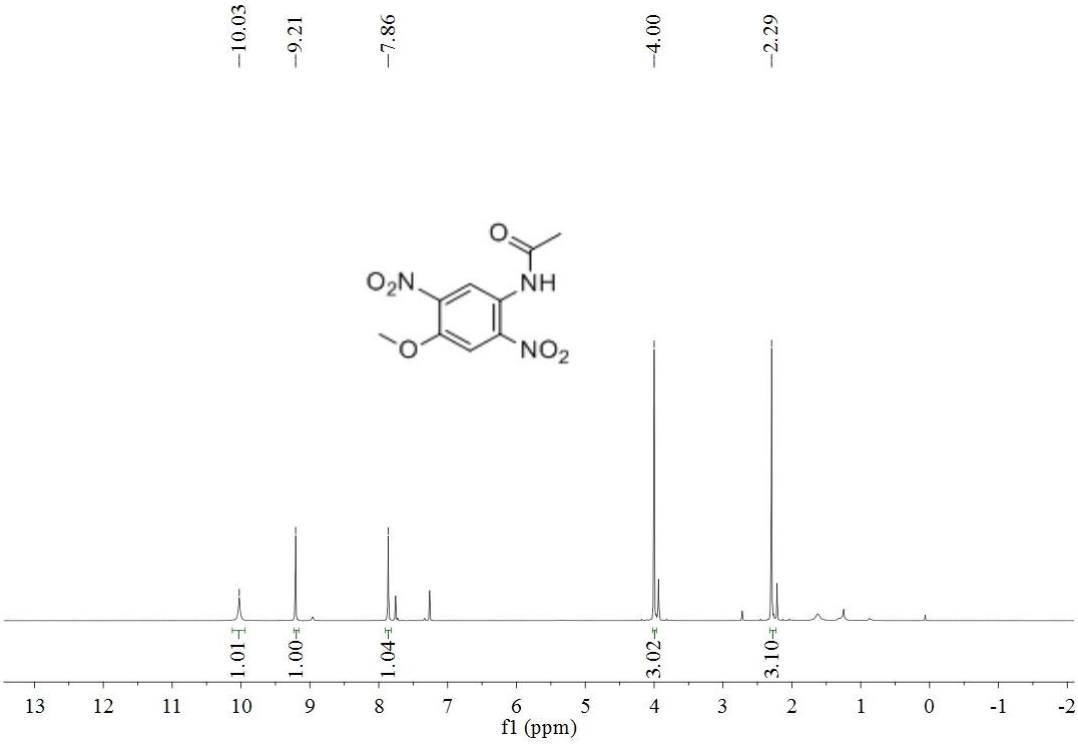


^{13}C NMR

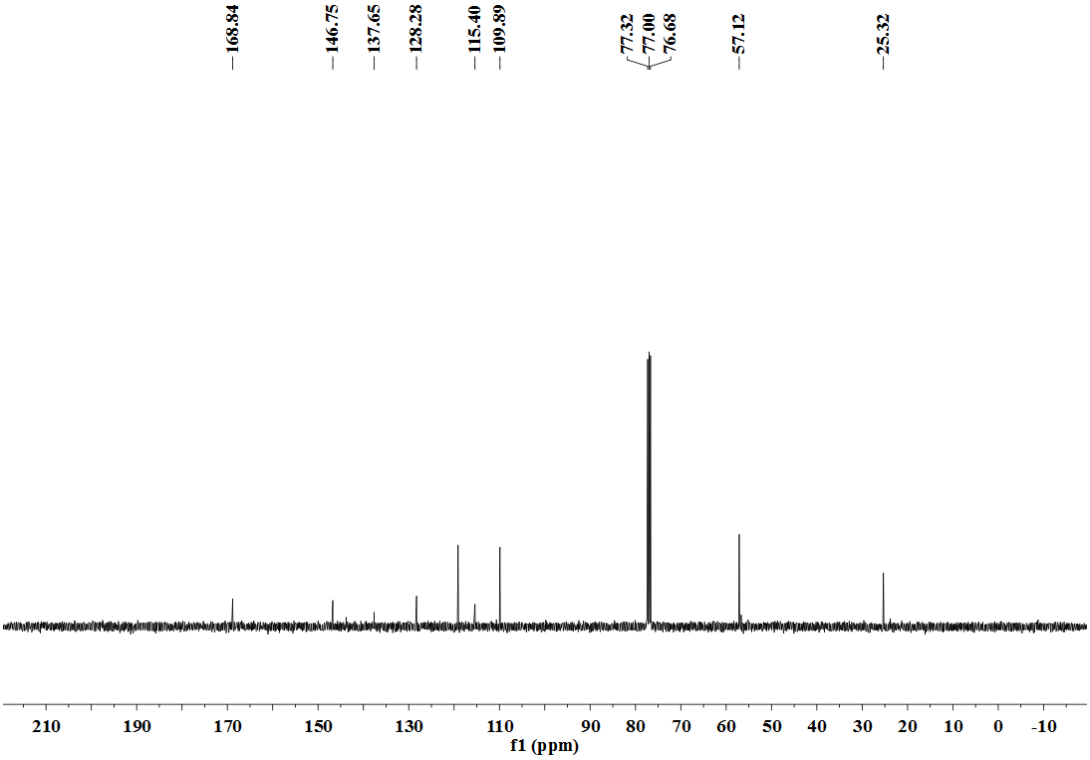


N-(4-Methoxy-2,5-dinitrophenyl)acetamide (2t)

^{1}H NMR

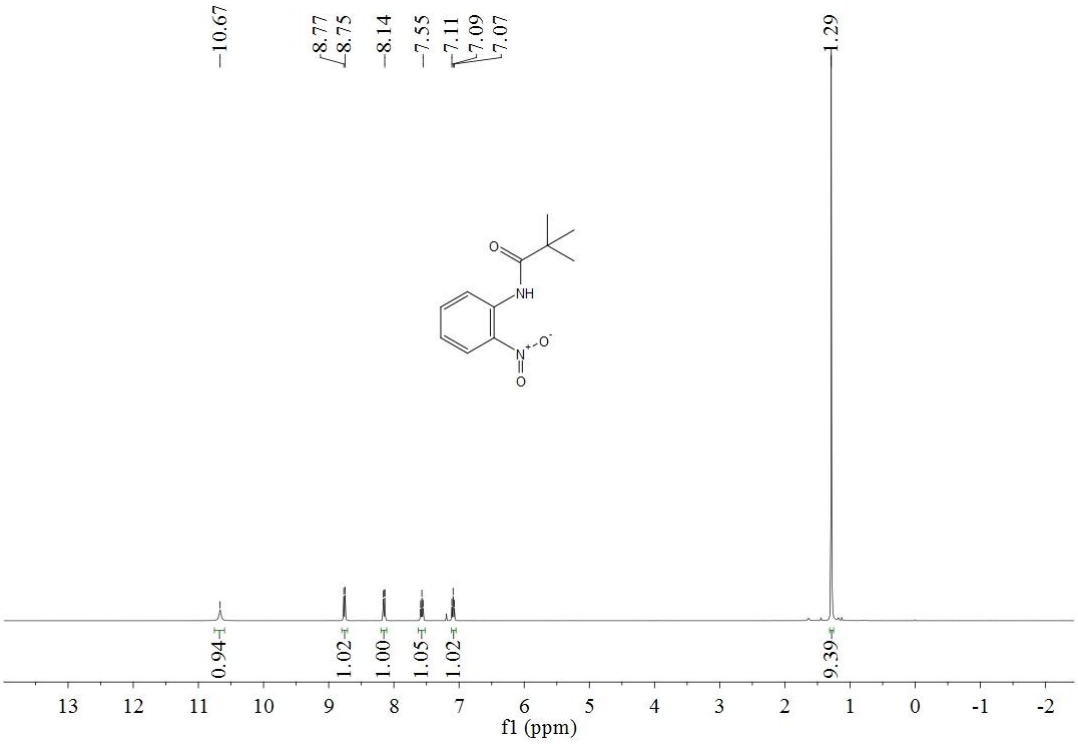


^{13}C NMR

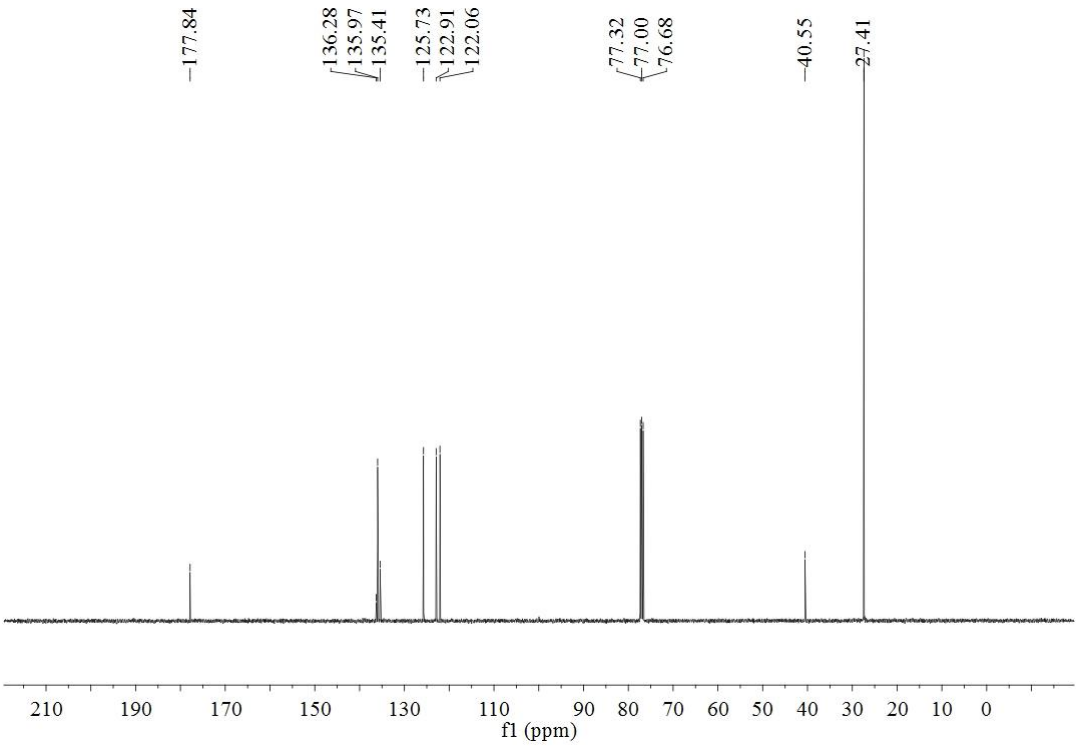


_N_-(2-Nitrophenyl)pivalamide (2u)

^{1}H NMR

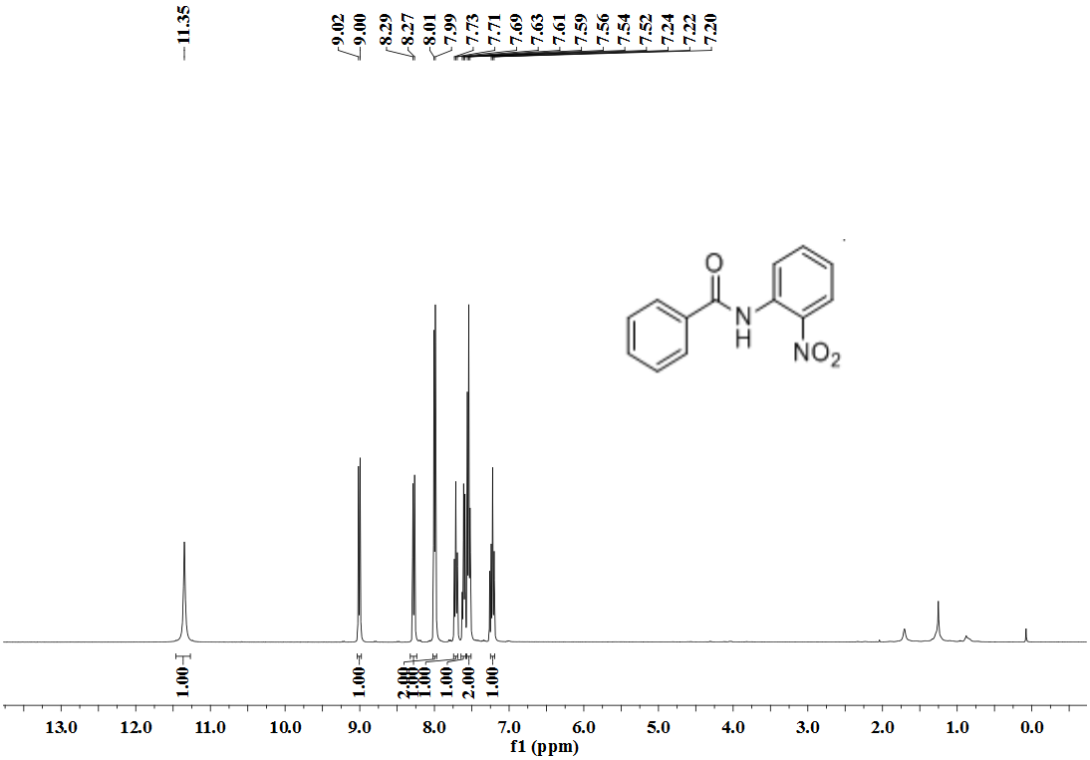


^{13}C NMR

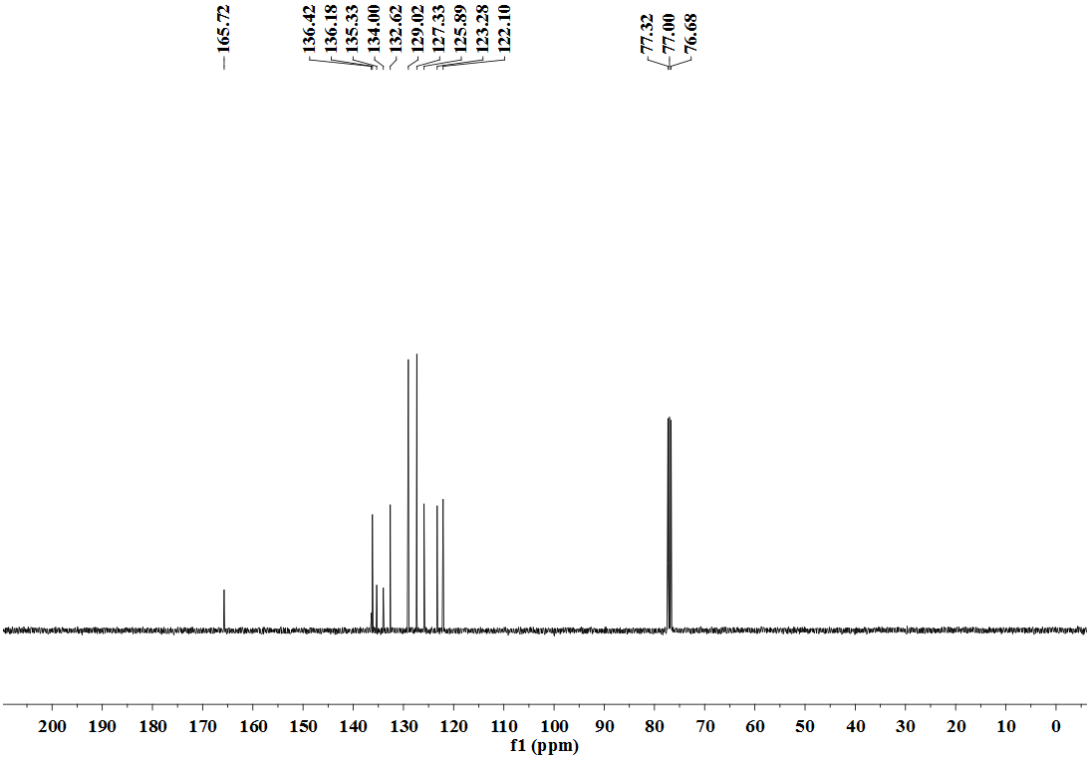


***N*-(2-Nitrophenyl)benzamide (2v)**

^{1}H NMR

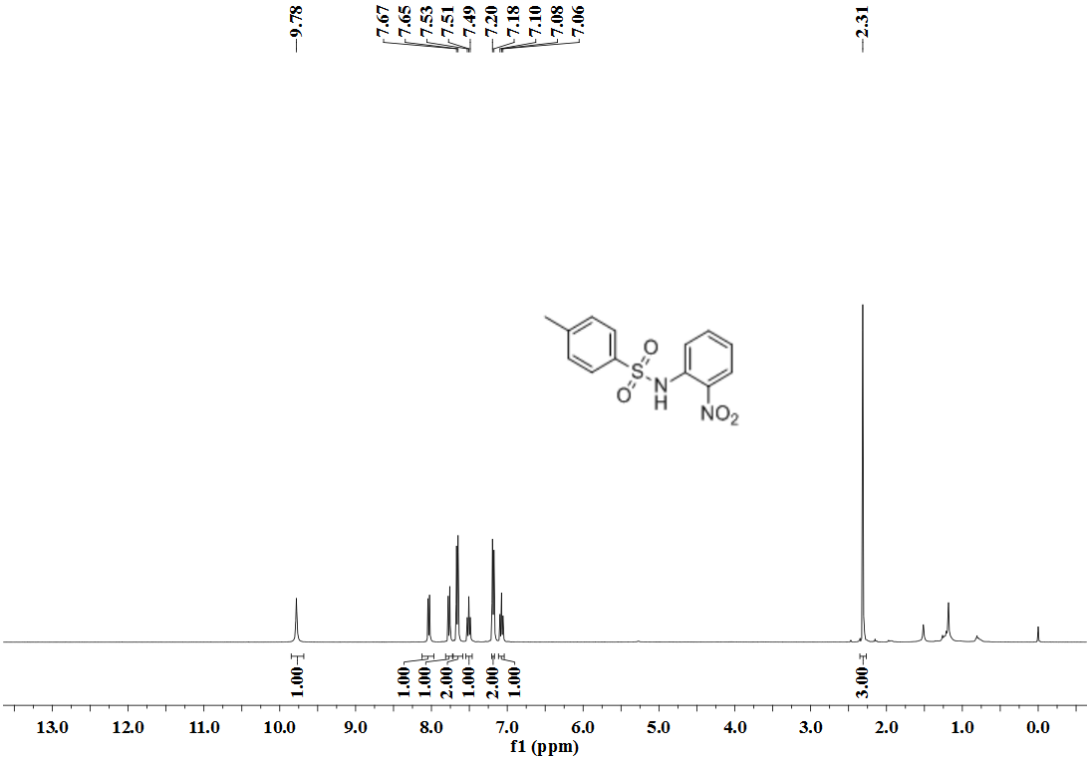


^{13}C NMR

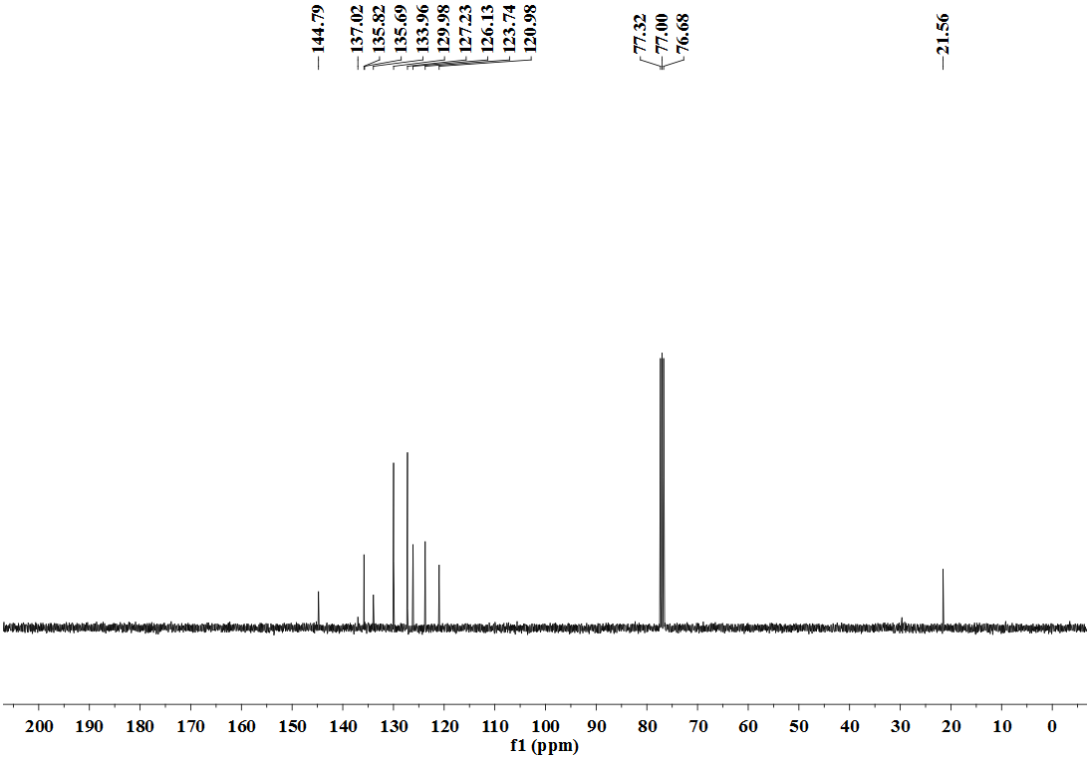


4-Methyl-*N*-(2-nitrophenyl)benzenesulfonamide (2w)

^{1}H NMR

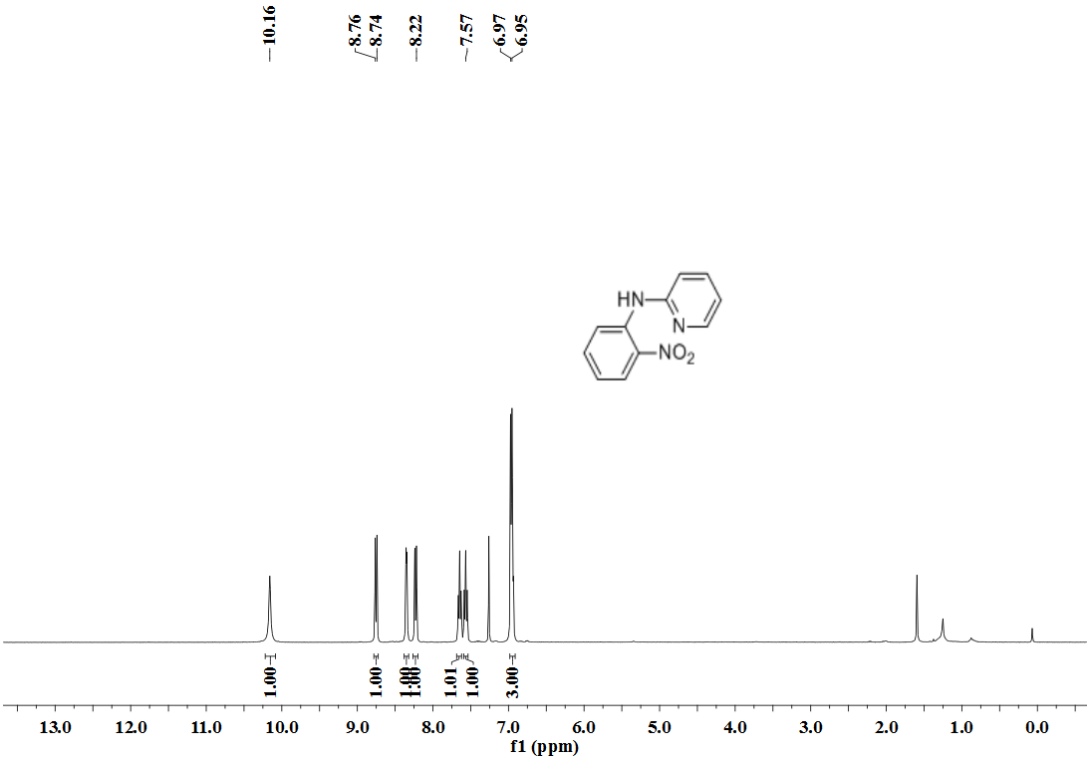


^{13}C NMR

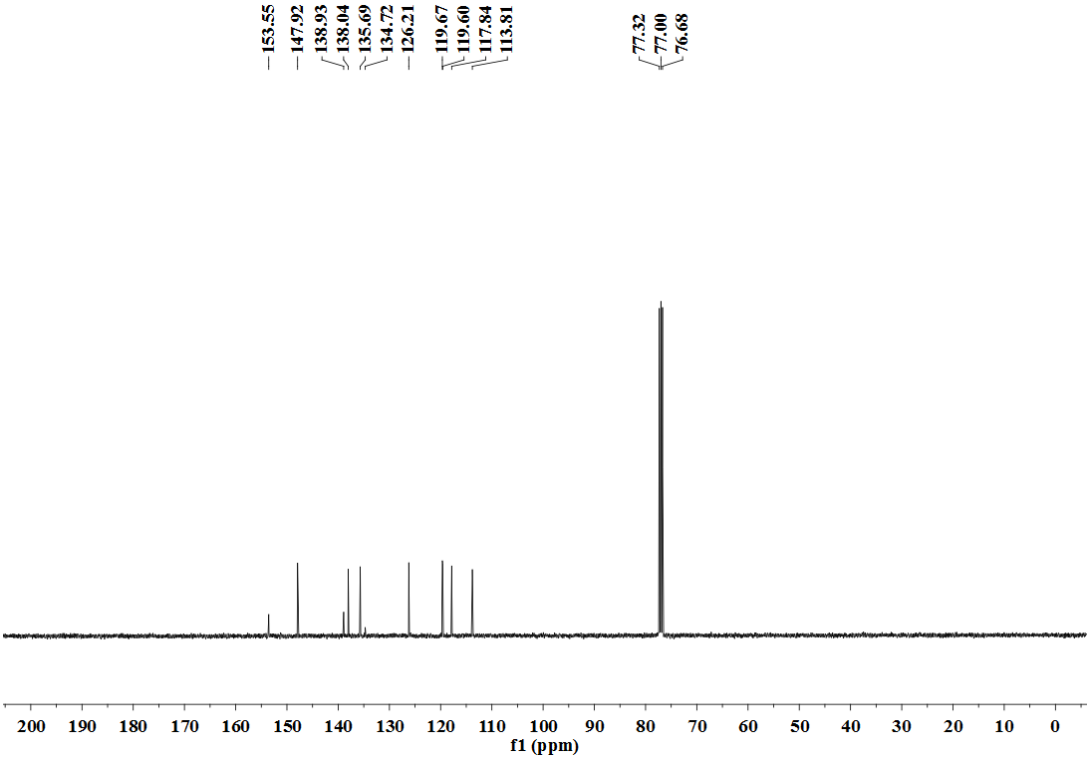


_N_-(2-Nitrophenyl)pyridin-2-amine (2x)

^{1}H NMR

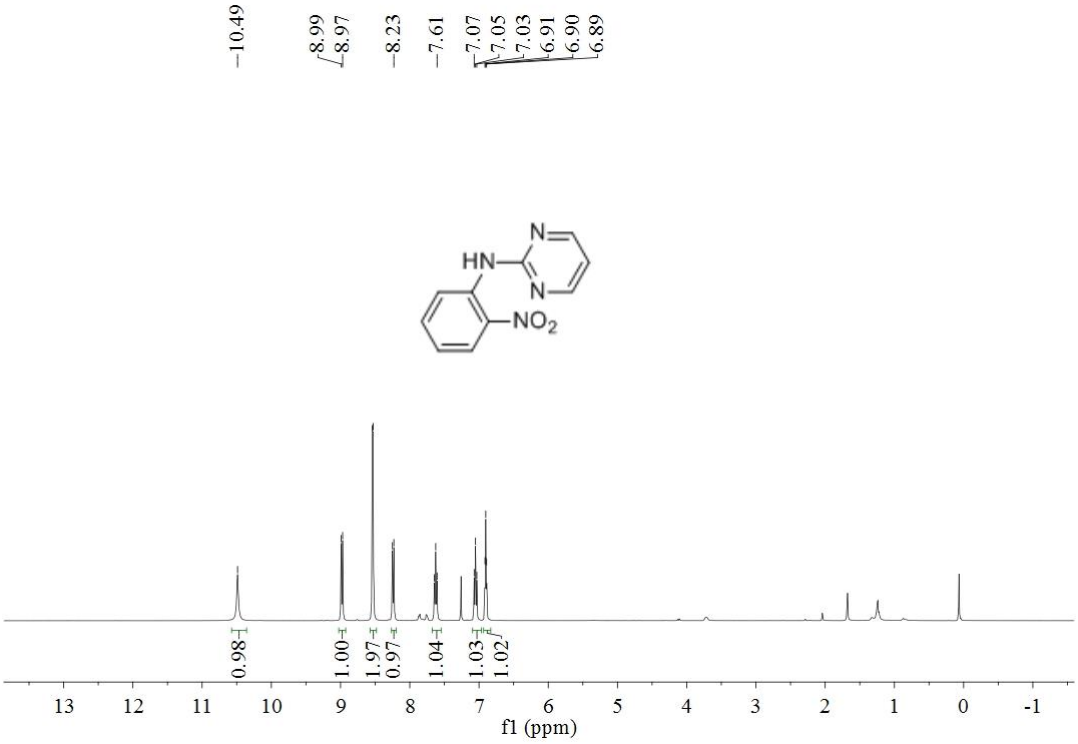


^{13}C NMR

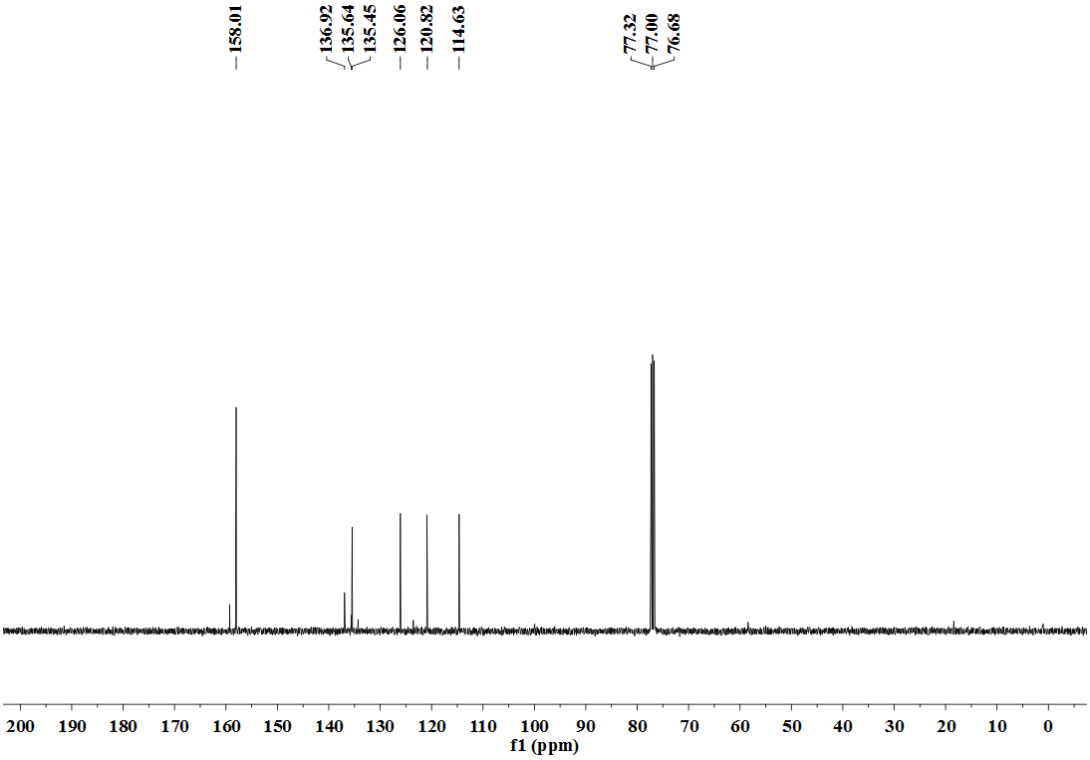


***N*-(2-Nitrophenyl)pyrimidin-2-amine (2y)**

^{1}H NMR

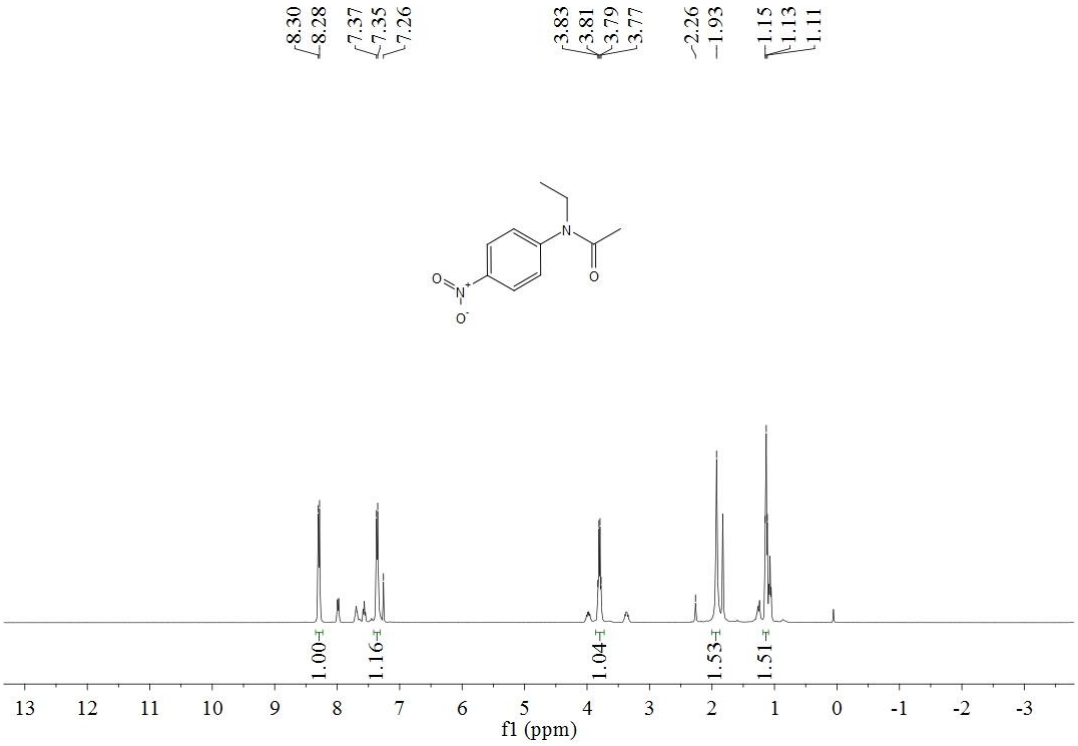


^{13}C NMR

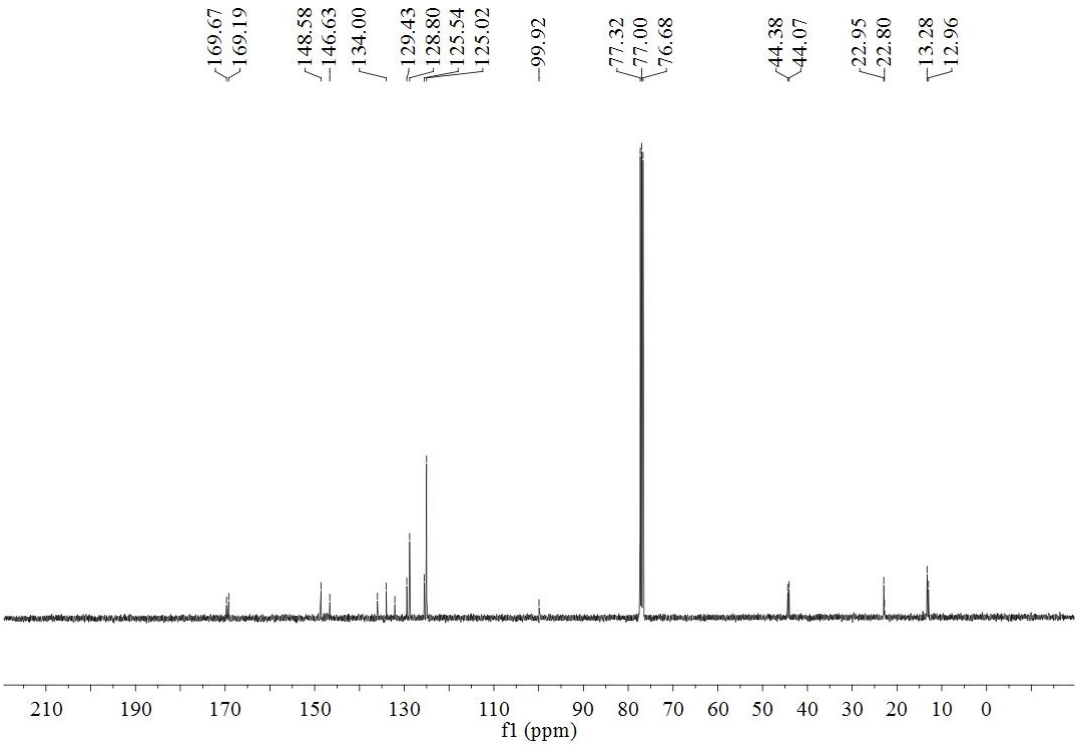


***N*-Ethyl-*N*-(4-nitrophenyl)acetamide (2z)**

^{1}H NMR

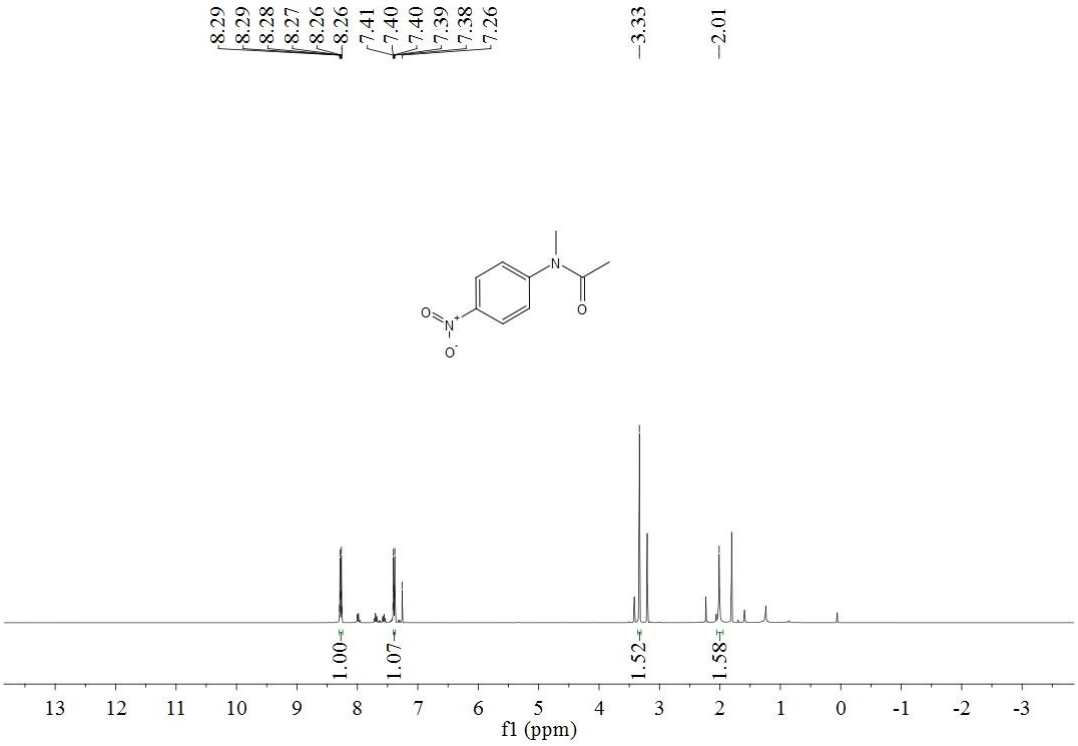


^{13}C NMR

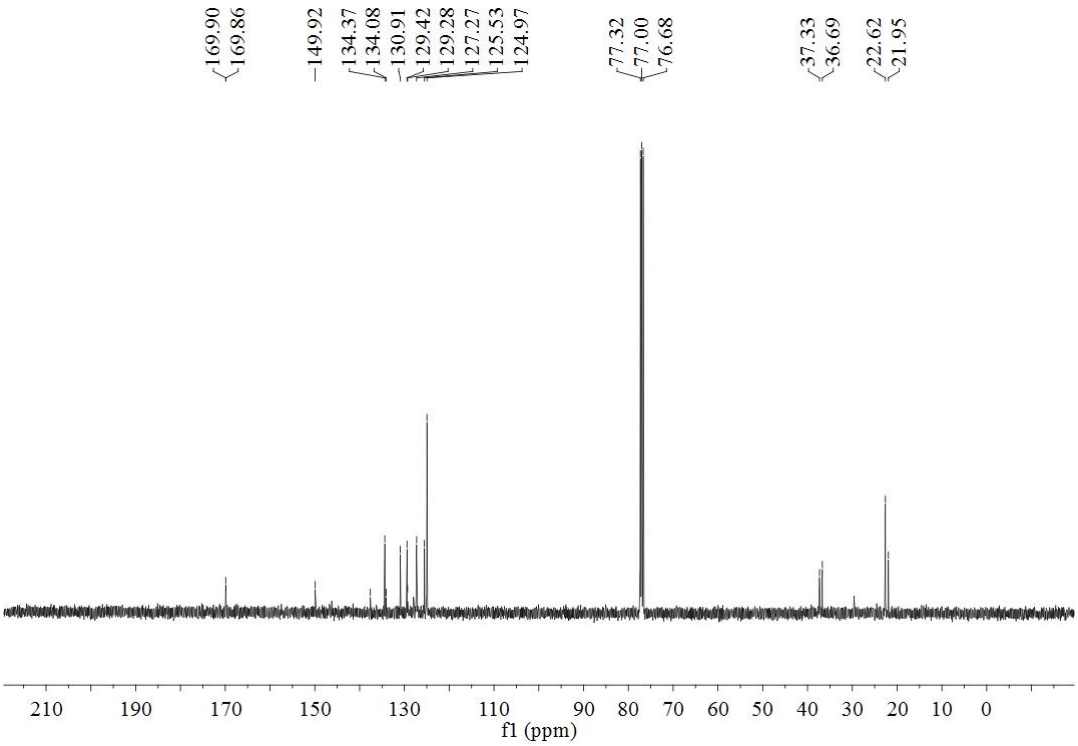


_N_-Methyl-_N_-(4-nitrophenyl)acetamide (2z')

^{1}H NMR

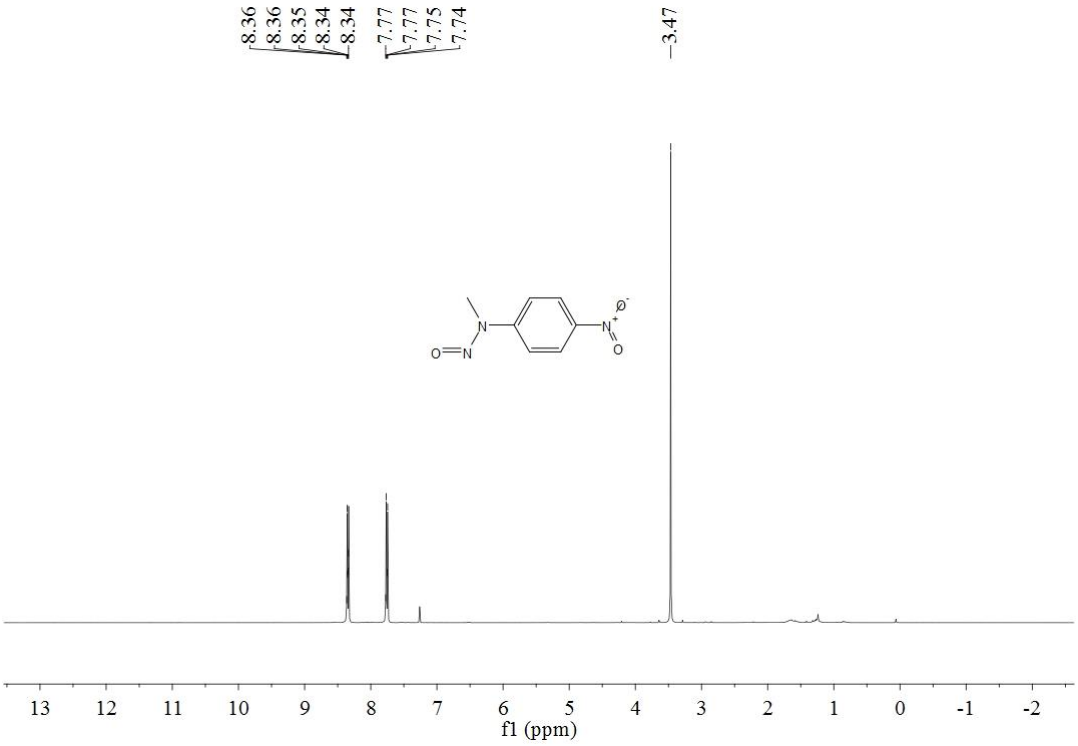


^{13}C NMR

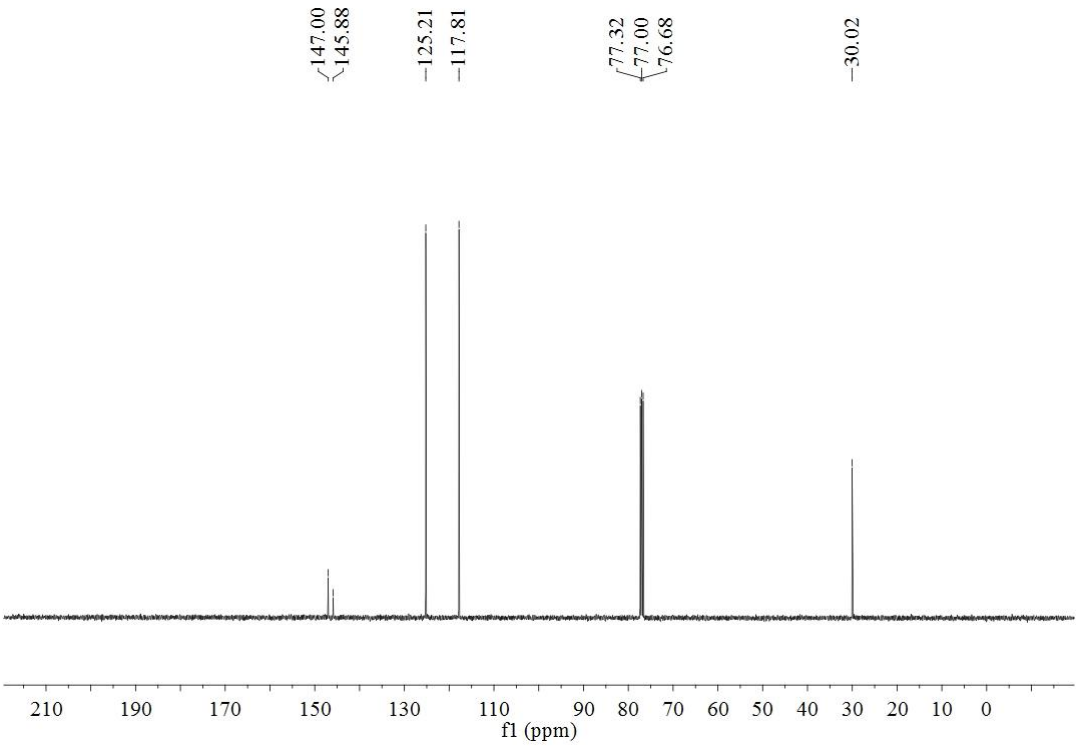


***N*-Methyl-4-nitroaniline (2aa)**

^{1}H NMR

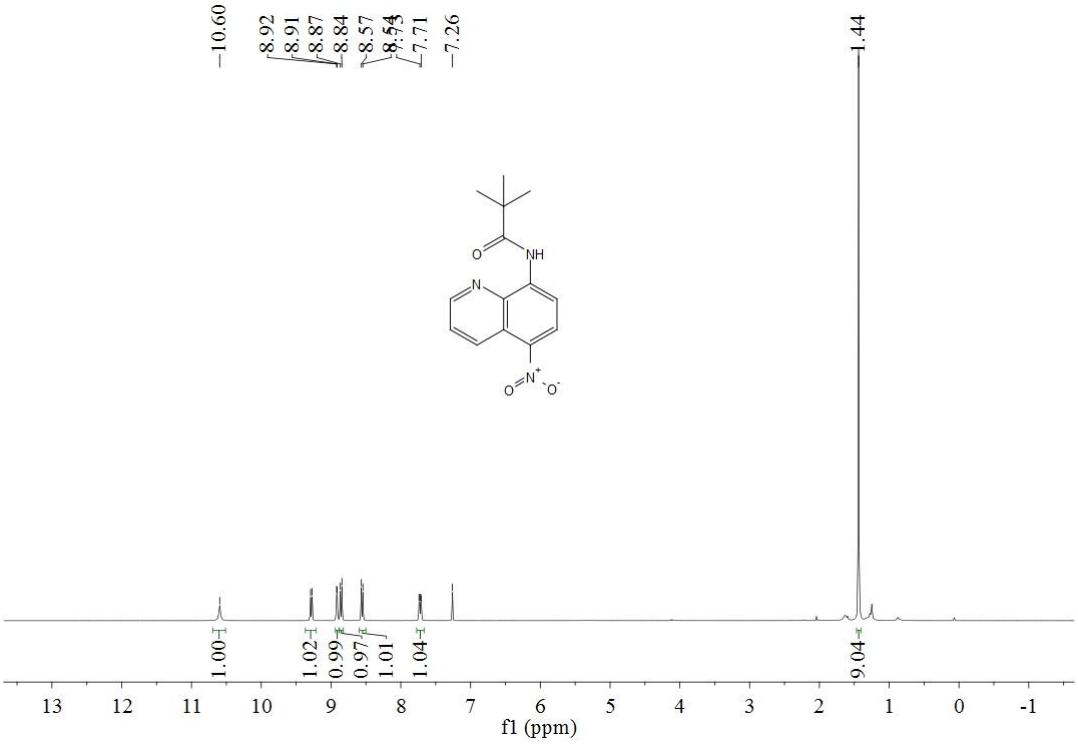


^{13}C NMR

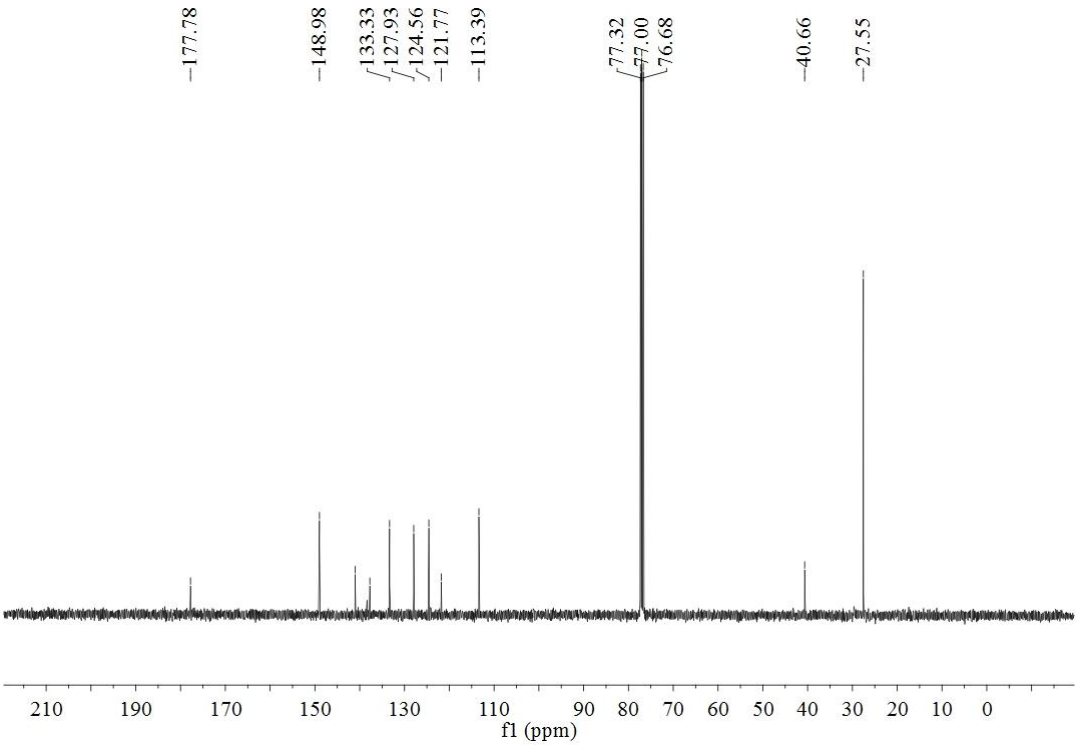


_N_-(5-Nitroquinolin-8-yl)pivalamide (2ab)

^{1}H NMR

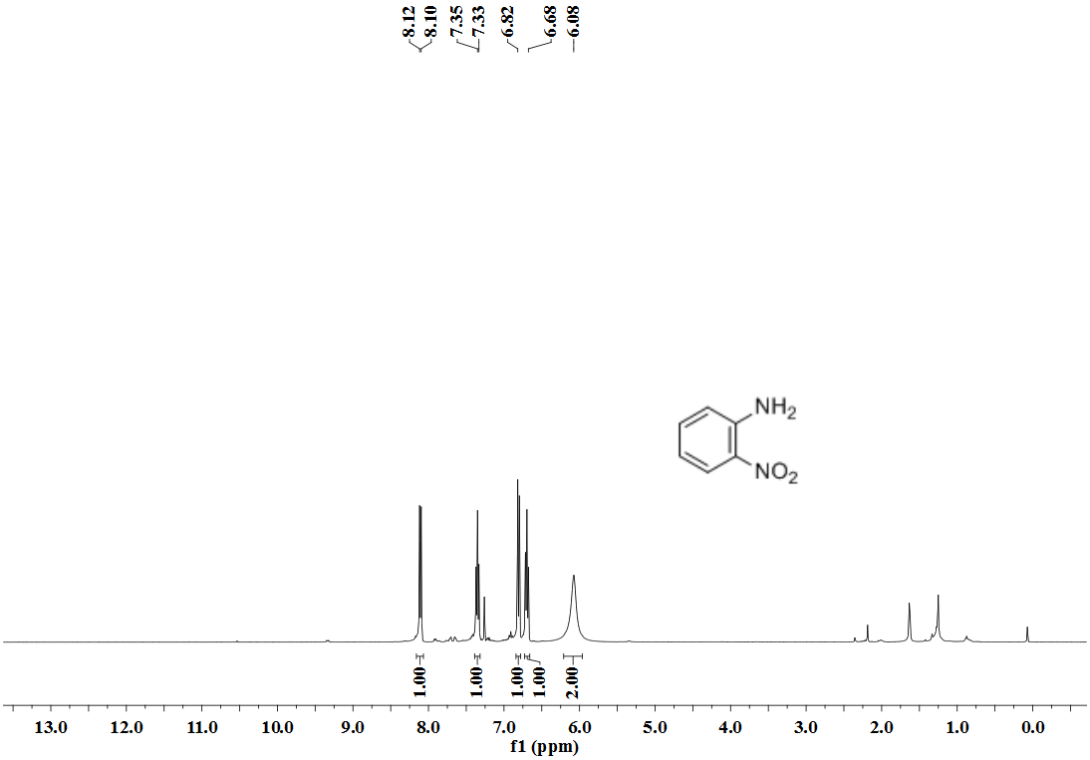


^{13}C NMR

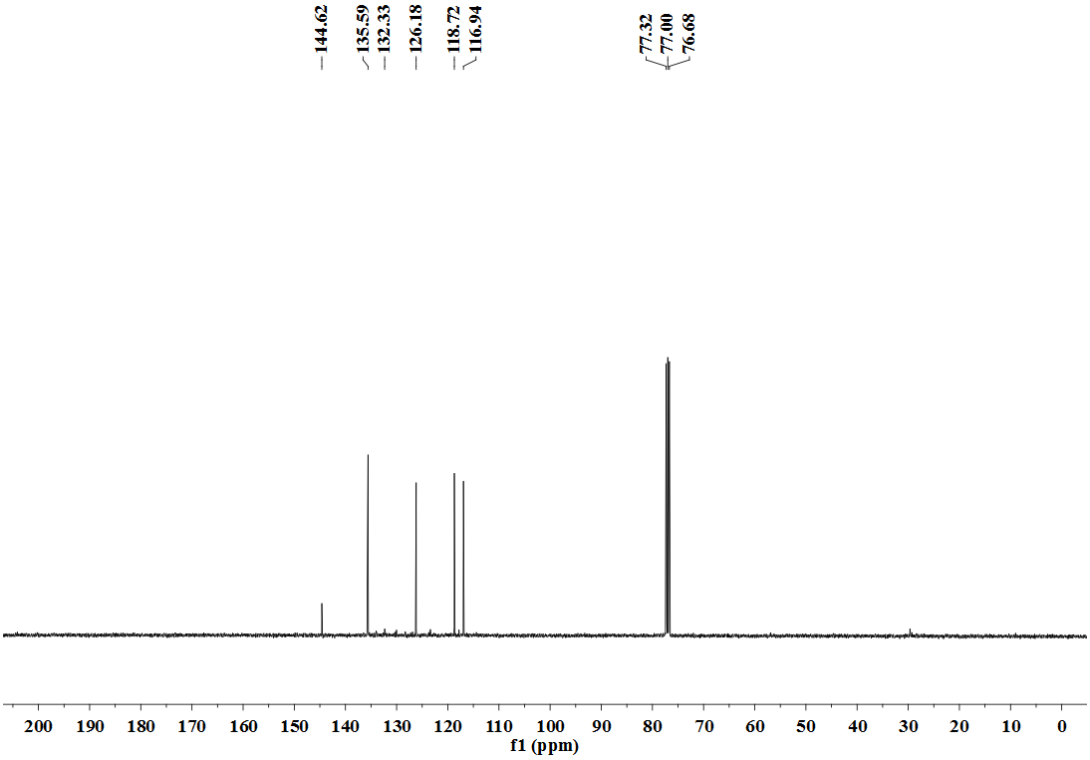


2-Nitroaniline (4)

^{1}H NMR

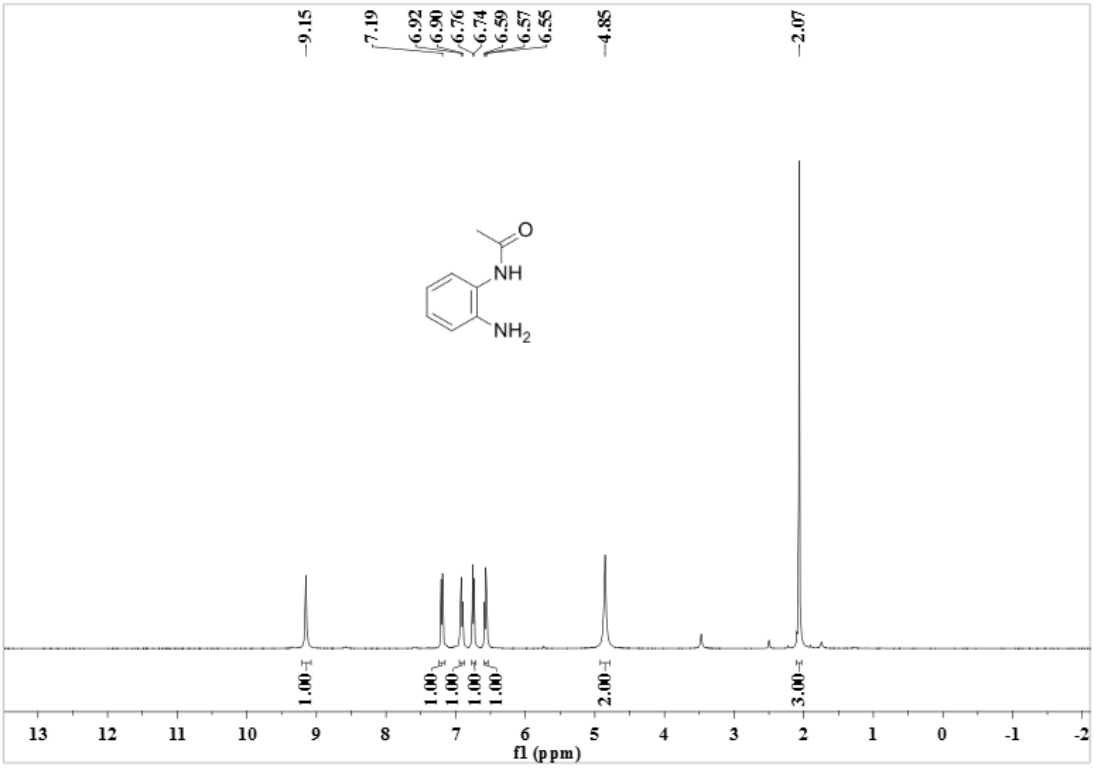


^{13}C NMR

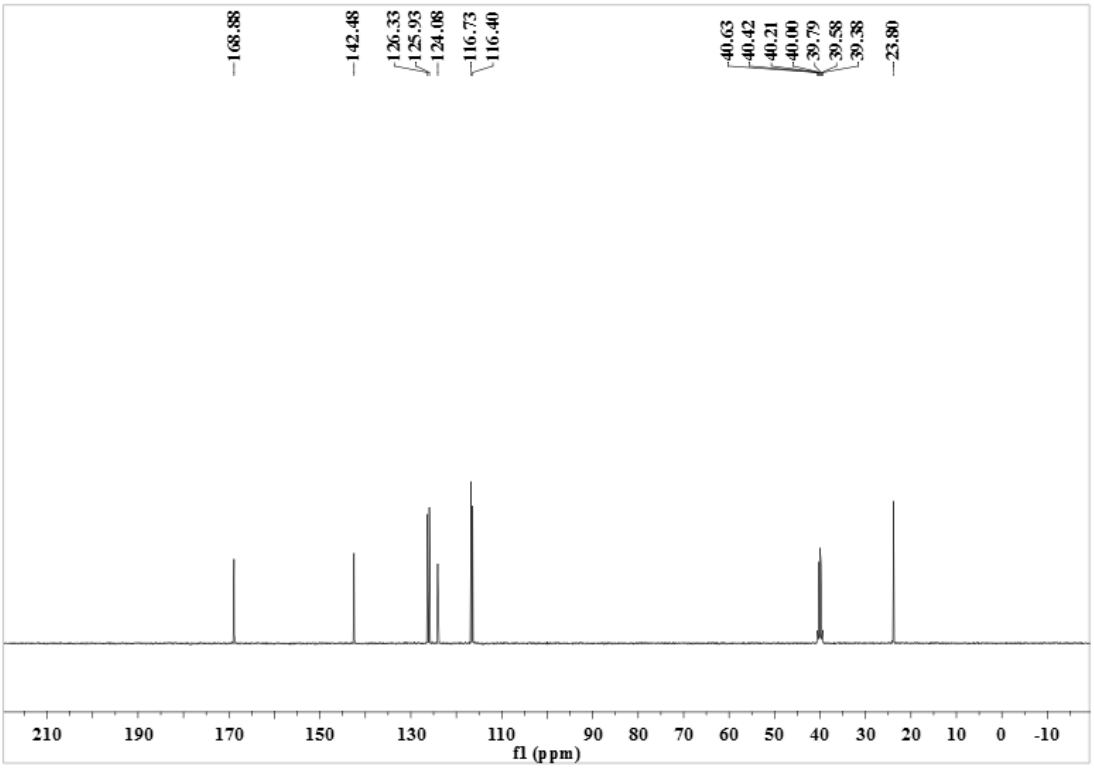


***N*-(2-Aminophenyl)acetamide (5)**

^{1}H NMR

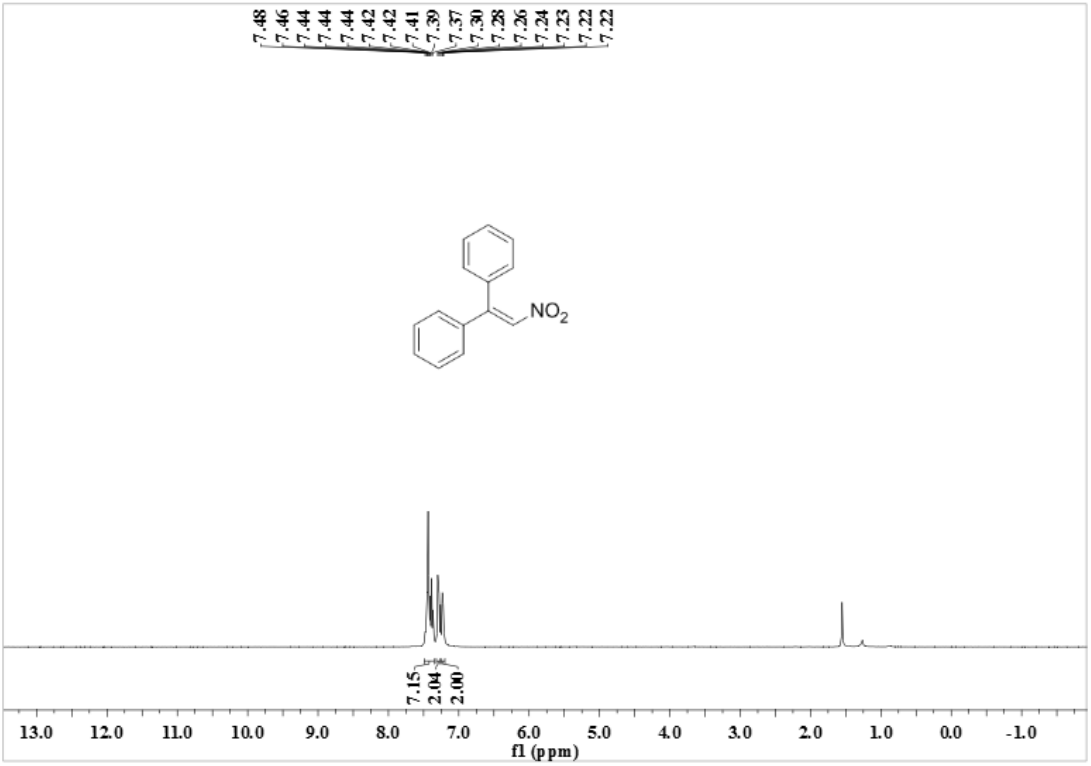
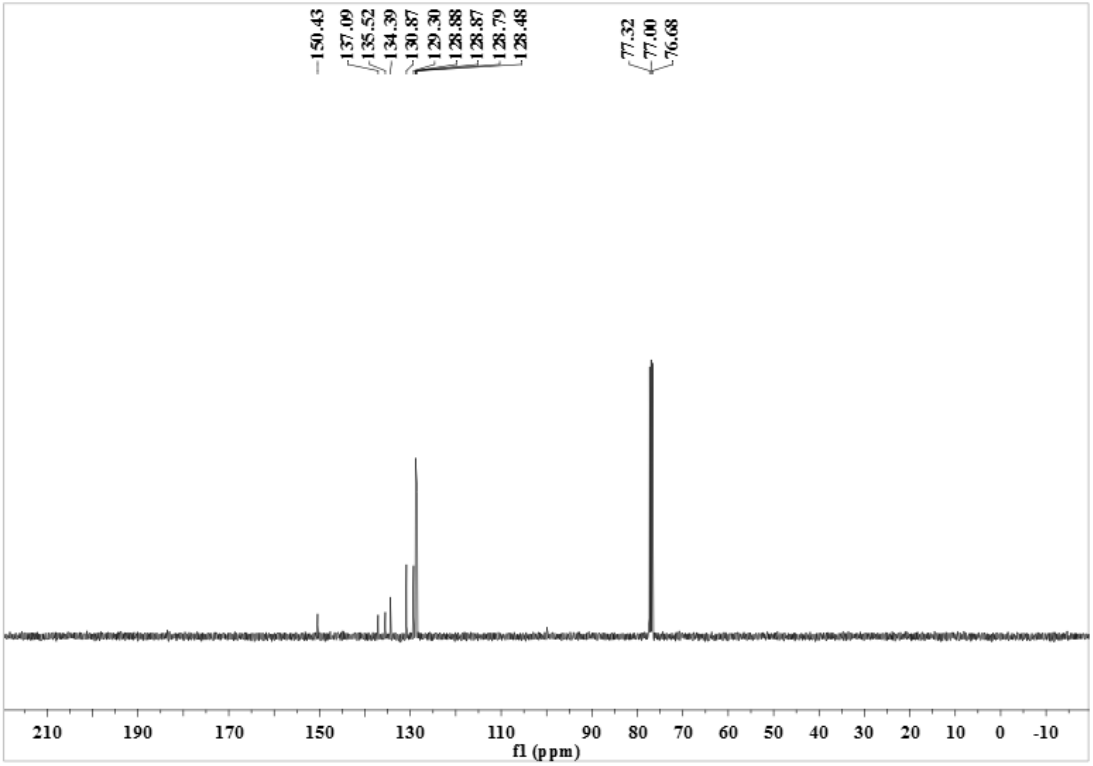


^{13}C NMR



(2-Nitroethene-1,1-diyl)dibenzene (6)

^{1}H NMR



^{13}C NMR