Catalyst-Free Generation of Acyl Radicals Induced by Visible Light in Water to Construct C-N Bonds

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Supporting Information

1. General experiments

NMR spectra were recorded on an Agilent-NMR-VNMRs 400 MHz spectrometer or Bruker Advance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) and referenced to $CDCl_3$ (7.26 ppm) or DMSO-d_6 (3.33 ppm) for ^{1}HNMR, and $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.52 ppm) for ^{13}CNMR. High-resolution mass spectrometry used electro-spraying ionization (ESI) on a Thermo Scientific LTQ Orbitrap XL. Column chromatography was performed with Qing Dao silica gel. Compounds **1** and **2a** were used directly as purchase. Compounds **2b**, **2c**, and **2e**–**2p** were prepared according to reported reference. [1] Compounds **2d**, **2r**-**2t** were prepared according to literature.[2] All data for these compounds were in consistent with references.[1],[2]

2. Mechanistic investigations

(1) UV-Vis absorption spectrum and reaction setup

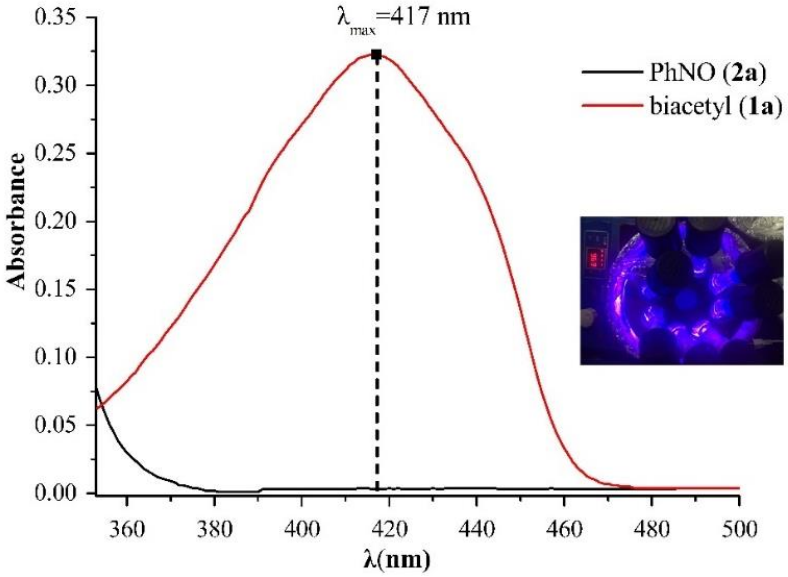
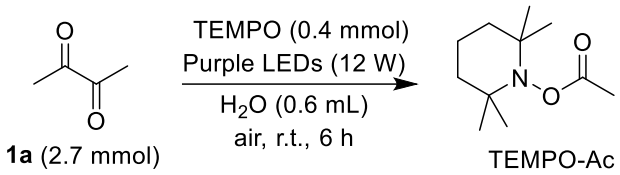


Figure S1. UV-Vis absorption spectrum of **1a** (4.5 mM) and **2a** (0.67 mM) in methanol; reaction setup (insert).

(2) Procedure for the reaction of 1a with TEMPO



To a 10 mL flask in air were added **1a** (2.7 mmol), TEMPO (0.4 mmol) and water (0.6 mL). The mixture was irradiated by purple LEDs (12 W) at room temperature for 6 h. The solution was concentrated. After purified by column chromatography, 10 mg TEMPO-Ac was obtained: yield 12%, white solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 3H), 1.70−1.20 (m, 6H), 1.13 (s, 6H), 1.04 (s, 6H). GC-MS (EI) m/z 199.0, 184.1, 157.1, 142.1, 126.1, 109.1. These data were in agreement with literature,[3] and the product has the same retention time as standard substance prepared according to literature[3] in GC-MS (EI).

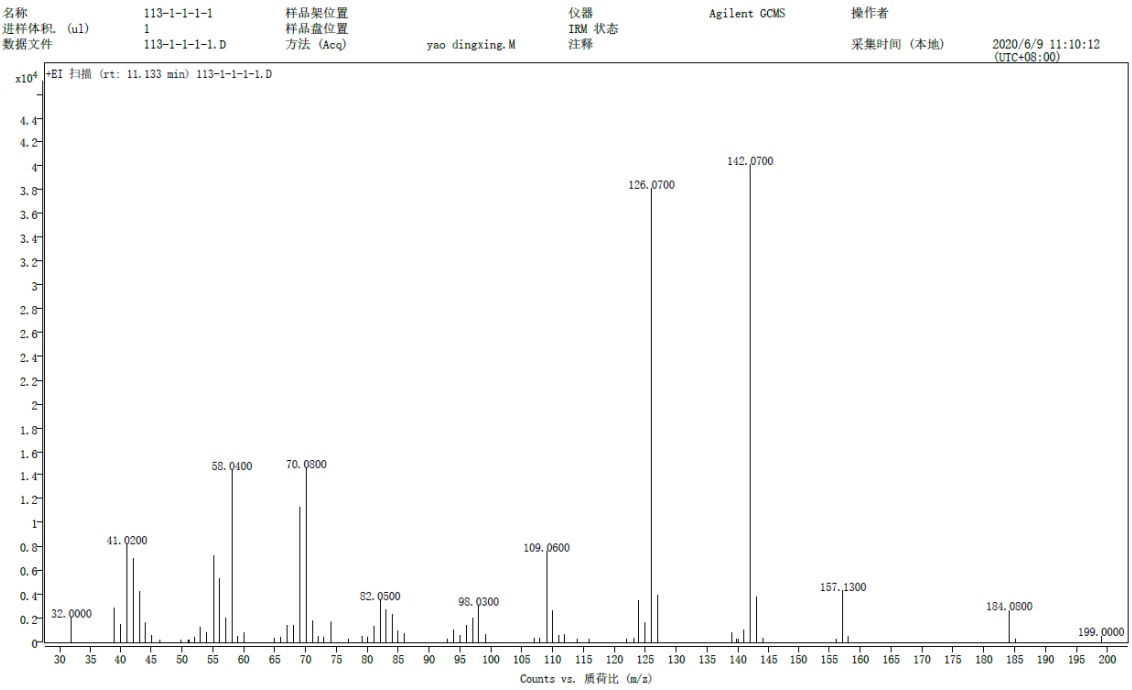


Figure S2. GC-MS (EI) spectrum of TEMPO-Ac.

(3) MS spectrum of compound 7

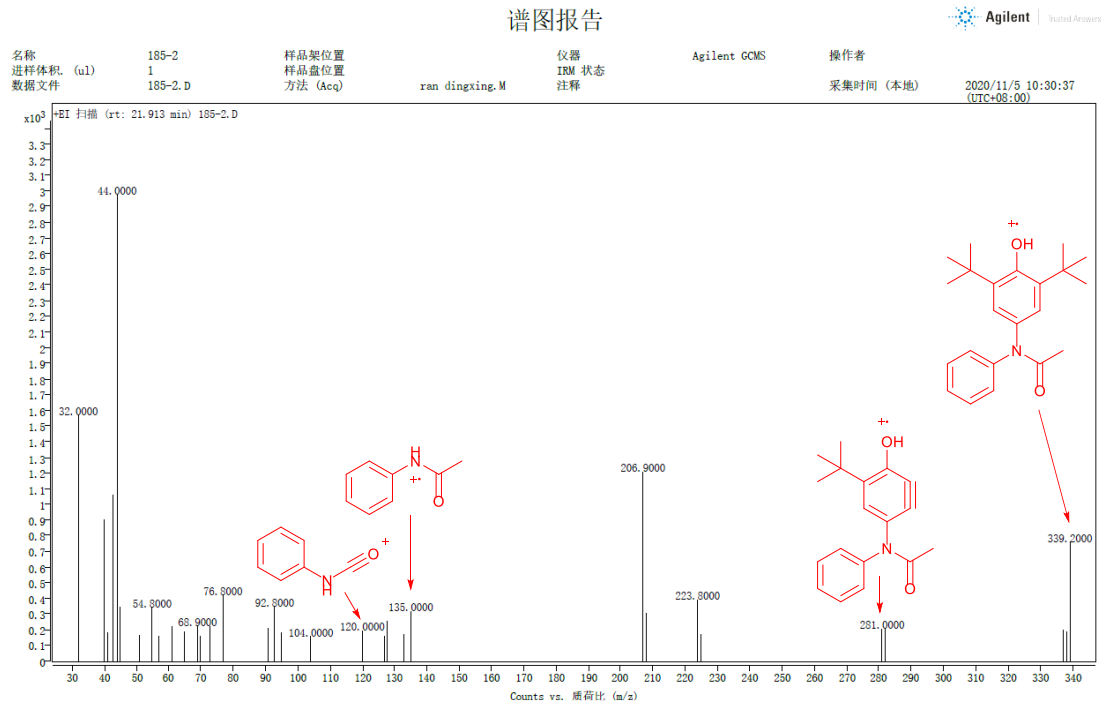


Figure S3. GC-MS (EI) spectrum of product **7** (possible fragment ions are shown in red).

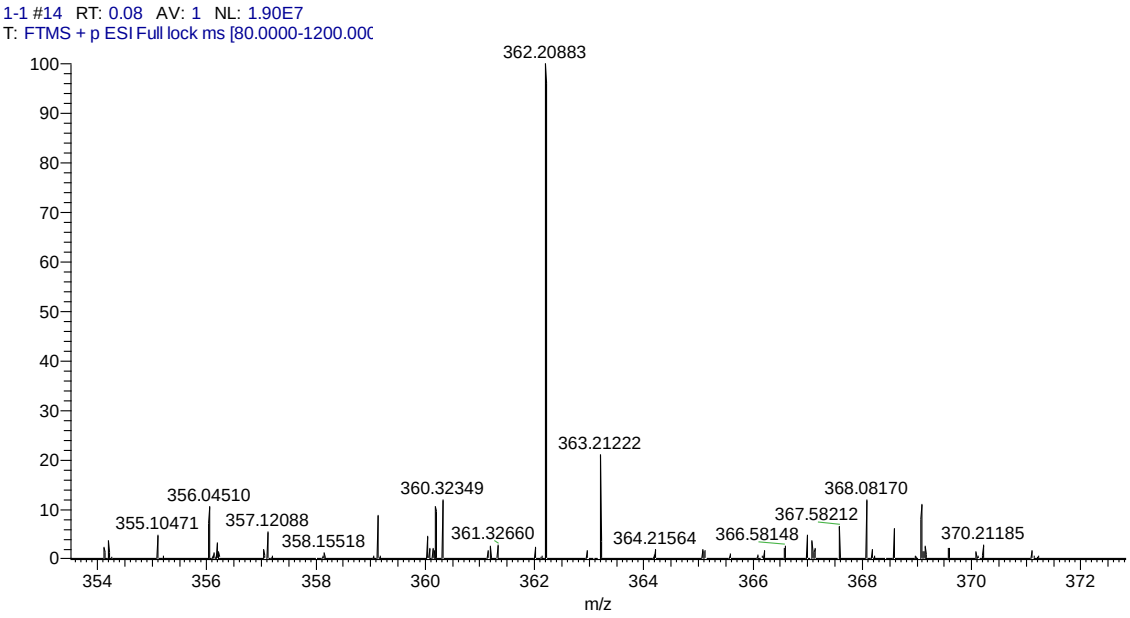


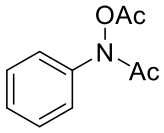
Figure S4. HR-MS (ESI) spectrum of product **7** (calcd for $C_{22}H_{29}NNaO_2^+$ $(M+Na)^+$ 362.2090, found 362.2088).

3. Procedures for the synthesis of 6 and 4

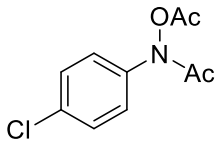
(1) Procedures for the synthesis of 6

To a 10 mL flask in air were added **1** (2.7 mmol), **2** (0.4 mmol), acetic acid (2.4 mmol) and water (0.6 mL). The mixture was irradiated by purple LEDs (12 W) at room temperature for 12 h. Then, the reaction mixture was extracted with DCM (5 mL*3). To the combined organic phases in a 25 mL flask was added NEt_3 (0.1 mmol) and acetyl chloride (0.6 mmol) at 0 ºC dropwise. Then the system was

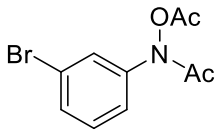
warmed to room temperature. After 1 h, the mixture was concentrated and purified by column chromatography with EtOAc/petroleum ether as eluen (1:5) to give product **6**.



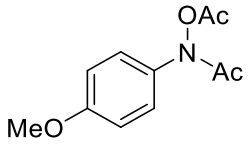
N-Acetoxy-*N*-phenylacetamide (**6a**)[4],[5]: yield 89%, white solid, m.p. 37.6-38.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.30 (m, 5H), 2.15 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 139.3, 129.4 (br), 21.4, 18.2.



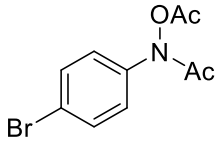
N-(Acetyloxy)-*N*-(4-chlorophenyl) acetamide (**6b**): yield 85%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 4H), 2.15 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 137.8, 129.5 (br), 21.3, 18.2.



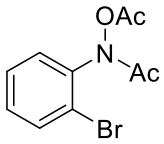
N-(Acetyloxy)-*N*-(3-bromophenyl) acetamide (**6c**)[4]: yield 84%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (t, J = 1.9 Hz, 1H), 7.50 – 7.36 (m, 2H), 7.28 (t, J = 8.0 Hz, 1H), 2.22 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 140.4, 130.5 (br), 122.5, 21.5, 18.3.



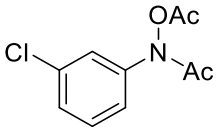
N-(Acetyloxy)-*N*-(4-methoxyphenyl) acetamide (**6d**): yield 91%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 3.77 (s, 3H), 2.23 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 137.8, 129.5 (br), 55.5, 21.4, 18.2.



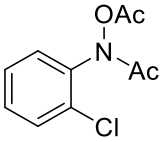
N-(Acetyloxy)-*N*-(4-bromophenyl) acetamide (**6e**)[5]: yield 84%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 2.18 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 138.3, 132.6 (br), 21.4, 18.3.



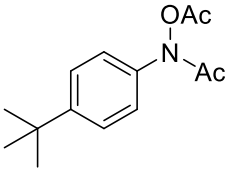
N-(Acetyloxy)-*N*-(2-bromophenyl) acetamide (**6f**)[6]: yield 80%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.52 (m, 2H), 7.46-7.35 (m, 1H), 7.35-7.25 (m, 1H), 2.15 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 166.2, 137.0, 132.3, 131.9, 130.8, 128.2 (br), 21.0, 18.4.



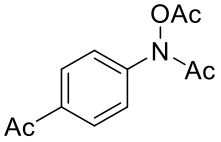
N-(Acetyloxy)-*N*-(3-chlorophenyl) acetamide (**6g**)[5]: yield 84%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s,1H), 7.44 – 7.23 (m, 3H), 2.26 (s, 3H), 2.14 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 140.2, 134.6, 130.2 (br), 21.4, 18.2.



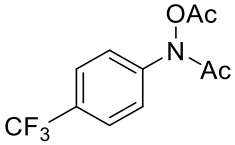
N-(Acetyloxy)-*N*-(2-chlorophenyl) acetamide (**6h**)[5]: yield 82%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.28 – 7.10 (m, 3H), 2.09 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 166.0, 136.5, 131.9 (br), 130.5, 127.4, 124.6, 21.5, 18.3.



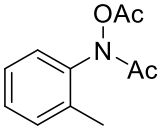
N-(Acetyloxy)-*N*-(4-tertiarybutylphenyl) acetamide (**6i**): yield 88%, white solid, m.p. 42.1-42.4 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.5 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 2.15 (s, 3H), 2.01 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 165.3, 136.5, 128.0 (br), 126.3 (br), 34.6, 31.0, 21.4, 18.1. HRMS (ESI) m/z calcd for $C_{14}H_{20}NO_3^+$ $(M+H)^+$ 250.1438, found 250.1440.



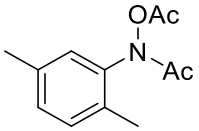
N-(Acetyloxy)-*N*-(4-acetophenone) acetamide (**6j**): yield 86%, white solid, m.p. 74.7-75.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 8.7 Hz, 2H), 2.57 (s, 3H), 2.25 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 167.9, 143.1, 129.4 (br), 26.7, 21.8, 18.4. HRMS (ESI) m/z calcd for $C_{12}H_{13}NO_4Na^+$ $(M+Na)^+$ 258.0737, found 258.0740.



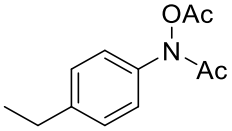
N-(Acetyloxy)-*N*-(4-trifluoromethylphenyl) acetamide (**6k**): yield 79%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 2.21 (s, 3H), 2.12 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 142.2, 126.3 (br), 123.7 (q, J = 270.3 Hz), 21.5, 18.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.49, -62.73. HRMS (ESI) m/z calcd for $C_{11}H_{11}F_3NO_3^+$ $(M+H)^+$ 262.0686, found 263.0687.



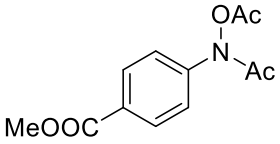
N-Acetoxy-*N*-(*o*-tolyl)acetamide (**6l**)[4]: yield 87%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.44 (m, 1H), 7.40-7.29 (m, 2H), 7.29-7.16 (m, 1H), 2.38 (s, 3H), 2.13 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 165.9, 137.8, 137.6, 131.2, 130.4, 129.9, 127.0, 20.8, 18.0, 17.3.



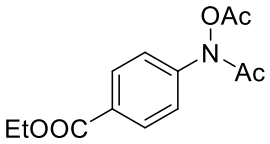
N-Acetoxy-*N*-(2,5-dimethylphenyl)acetamide(**6m**): yield 92%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.20-7.07 (m, 2H), 2.30 (s, 6H), 2.14 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 166.1, 137.9, 137.2, 134.6, 131.4, 131.2, 130.5, 21.2, 20.7, 18.4, 17.1.



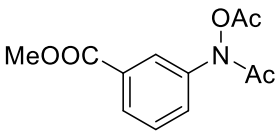
N-Acetoxy-*N*-(4-ethylphenyl)acetamide(**6n**): yield 90%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 2.64 (q, J = 7.2 Hz, 2H), 2.14 (s, 3H), 2.01 (s, 3H), 1.21 (t, J = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 165.0, 145.8, 136.3, 128.3 (br), 123.6 (br), 27.7, 20.7, 17.4, 14.7. HRMS (ESI) m/z calcd for $C_{12}H_{15}NO_3Na^+$ $(M+Na)^+$ 244.0944, found 244.0944.



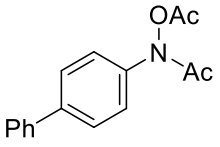
Methyl 4-(*N*-acetoxyacetamido)benzoate(**6o**): yield 93%, white solid, m.p. 79.5-80.0^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 3.90 (s, 3H), 2.25 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 166.2, 143.1, 130.7 (br), 52.4, 21.8, 18.4. HRMS (ESI) m/z calcd for $C_{12}H_{13}NO_5Na^+$ $(M+Na)^+$ 274.0686, found 274.0686.



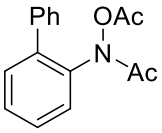
Ethyl 4-(*N*-acetoxyacetamido)benzoate (**6p**): yield 94%, white solid, m.p. 90.9-91.7 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.7 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 2.24 (s, 3H), 2.13 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 167.7, 143.0, 130.7 (br), 61.3, 21.8, 18.4, 14.4. HRMS (ESI) m/z calcd for $C_{13}H_{15}NO_5Na^+$ $(M+Na)^+$ 288.0842, found 288.0843.



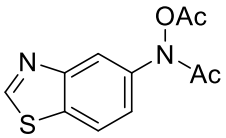
Methyl 3-(*N*-acetoxyacetamido)benzoate (**6q**): yield 90%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 8.00-7.90 (m, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 6.9 Hz, 1H), 3.89 (s, 3H), 2.20 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 165.7, 139.3, 131.2, 129.3 (br), 52.2, 21.3, 18.1. HRMS (ESI) m/z calcd for $C_{12}H_{13}NO_5Na^+$ $(M+Na)^+$ 274.0686, found 274.0686.



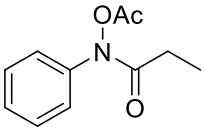
N-([1, 1'-Biphenyl]-4-yl)-*N*-acetoxyacetamide (**6r**): yield 75%, white solid, m.p. 115.1-115.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.45 (t, J = 8.2Hz, 2H), 7.37 (t, J = 12 Hz, 1H), 2.22 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 139.8, 138.4, 129.0, 128.1 (br), 128.0 (br), 127.2, 21.6, 18.4.



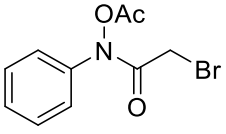
N-([1,1'-Biphenyl]-2-yl)-*N*-acetoxyacetamide (**6s**): yield 72%, white solid, m.p. 94.9-95.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 6.3 Hz, 1H), 7.60-7.32 (m, 8H), 2.21 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 165.1, 142.1, 137.8, 136.8, 131.3, 130.9, 130.7 (br), 128.8 (br), 128.2, 20.9, 18.5.



N-Acetoxy-*N*-(benzo[d]thiazol-5-yl) acetamide (**6t**): yield 77%, white solid, m.p. 80.1-80.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.19 (s, 1H), 7.98 (d, J = 8.6 Hz, 1H), 7.59 (d, J = 8.6 Hz, 1H), 2.19 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 156.1, 153.7, 137.9, 122.6 (br), 21.6, 18.4. HRMS (ESI) m/z calcd for $C_{11}H_{11}N_2O_3S^+$ $(M+H)^+$ 251.0485, found 251.0488.



N-Acetoxy-*N*-phenylpropionamide (**6u**): yield 44%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.26 (m, 5H), 2.25 (br, 2H), 2.16 (s, 3H), 1.11 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 138.9, 129.0 (br), 26.3, 17.7, 8.4. HRMS (ESI) m/z calcd for $C_{11}H_{14}NO_3^+$ $(M+H)^+$ 208.0968, found 208.0970.

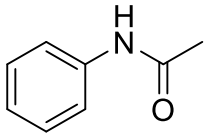


N-Acetoxy-2-bromo-*N*-phenylacetamide (**6v**): yield 57%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 5H), 3.74 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 167.0, 161.6, 137.8, 130.4, 129.4, 128.2, 123.0, 20.3, 17.7. HRMS (ESI) m/z calcd for $C_{10}H_{10}BrNO_3Na^+$ $(M+Na)^+$ 293.9736, found 293.9739.

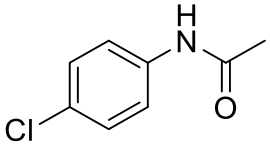
(2) Procedures for the reaction of 1 and 2 in the synthesis of 4

To a 10 mL flask in water (0.6 mL) and acetone (3 mL) at room temperature were added **1** (1.1 mmol), **2** (0.4 mmol) and NaCl (0.8 mmol, 47 mg) under argon. The reaction mixture was irradiated by purple LEDs

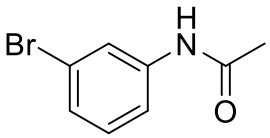
(12 W) at room temperature for 12 h. Then, the reaction mixture was extracted with DCM (5 mL*3). The organic phases were combined and dried over anhydrous Na_2SO_4 for 1 hour. After that the filtrate was concentrated and purified by column chromatography with EtOAc/petroleum ether as eluen (1:5) to give product **4**.



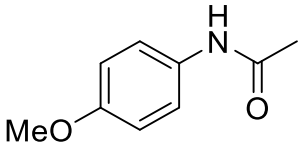
N-Phenylacetamide (**4a**)[7]: yield 76%, white solid, m.p. 113.9-114.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.89 (s, 1H), 7.53 (d, J = 7.9 Hz, 2H), 7.24 (t, J = 7.9 Hz, 2H), 6.98 (t, J = 7.4 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.3, 139.4, 128.7, 123.0, 119.0, 24.0.



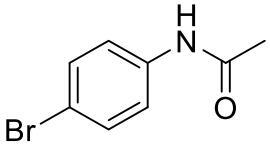
N-(4-Chlorophenyl)acetamide (**4b**)[8]: yield 68%, white solid, m.p. 177.1-178.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.05 (s, 1H), 7.58 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.5, 138.3, 128.6, 126.5, 120.5, 24.0.



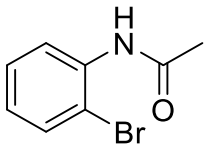
N-(3-Bromophenyl)acetamide (**4c**)[9]: yield 67%, white solid, m.p. 77.7-78.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.09 (s, 1H), 7.93 (s, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.26 – 7.18 (m, 2H), 2.03 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.7, 140.9, 130.7, 125.6, 121.6, 121.2, 117.7, 24.1.



N-(4-Methoxyphenyl)acetamide (**4d**)[7]: yield 72%, white solid, m.p. 125.4-126.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.75 (s, 1H), 7.47 (d, J = 9.0 Hz, 1H), 6.85 (d, J = 9.0 Hz, 1H), 3.70 (s, 3H), 1.99 (s, 3H);^{13}C NMR (101 MHz, DMSO-d_6) δ 167.8, 155.0, 132.6, 120.5, 113.8, 55.1, 23.8.

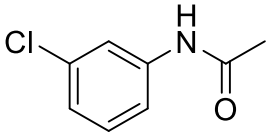


N-(4-Bromophenyl)acetamide (**4e**)[7]: yield 67%, white solid, m.p. 166.5-166.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.05 (s, 1H), 7.53 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 2.01 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.5, 138.7, 131.5, 120.9, 114.5, 24.1.

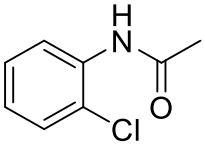


N-(2-Bromophenyl)acetamide (**4f**)[10]: yield 62%, white solid, m.p. 95.6-96.0 °C; ^{1}H NMR (400

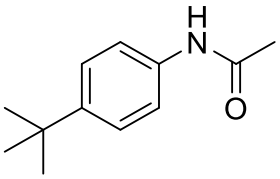
MHz, DMSO-d_6) δ 9.46 (s, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.5, 136.4, 132.6, 127.9, 127.3, 126.9, 117.9, 23.3.



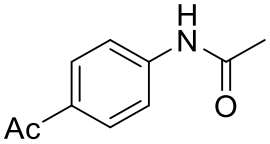
N-(3-Chlorophenyl)acetamide (**4g**)[7]: yield 65%, white solid, m.p. 68.5-69.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.09 (s, 1H), 7.76 (s, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.26 (t, J = 8.1 Hz, 1H), 7.03 (d, J = 7.9 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.6, 140.7, 133.0, 130.3, 122.6, 118.4, 117.3, 24.0.



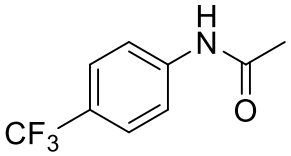
N-(2-Chlorophenyl)acetamide (**4h**)[7],[10]: yield 61%, white solid, m.p. 83.2-83.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.46 (s, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.42 (dd, J = 8.0 Hz, 1H), 7.26 (td, J = 7.9, 1.3 Hz, 1H), 7.12 (td, J = 8.2, 2.0 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.6, 135.1, 129.4, 127.3, 126.4, 126.2, 126.1, 23.3.



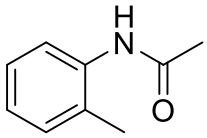
N-(4-(Tert-butyl)phenyl)acetamide (**4i**)[11]: yield 75%, white solid, m.p. 168.2-169.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.82 (s, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H), 1.99 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.1, 145.2, 136.8, 125.3, 118.8, 34.0, 31.2, 24.0.



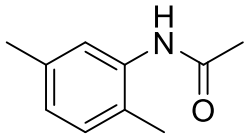
N-(4-Acetylphenyl)acetamide (**4j**)[12]: yield 70%, white solid, m.p. 169.2-170.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.21 (s, 1H), 7.86 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H), 2.46 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.4, 168.9, 143.7, 131.5, 129.4, 118.1, 26.4, 24.2.



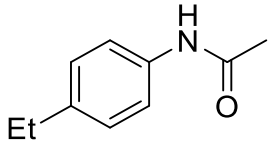
N-(4-(Trifluoromethyl)phenyl)acetamide (**4k**)[13]: yield 64%, white solid, m.p. 105.5-106.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.23 (s, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 2.03 (s, 3H);^{13}C NMR (101 MHz, DMSO-d_6) δ 169.0, 142.8, 126.0 (q, J = 3.8 Hz), 124.4 (q, J = 272.1 Hz), 123.0 (q, J = 32.0 Hz), 118.8, 24.1; ^{19}F NMR (376 MHz, DMSO-d_6) δ -60.33.



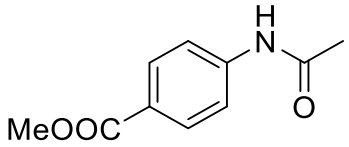
N-(*o*-Tolyl)acetamide (**4l**)[7]: yield 78%, white solid, m.p. 103.9-104.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.25 (s, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.17 (d, J = 7.3 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 7.04 (t, J = 7.3 Hz, 1H), 2.17 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.7, 135.9, 132.2, 130.4, 129.1, 125.5, 122.5, 20.5, 17.0.



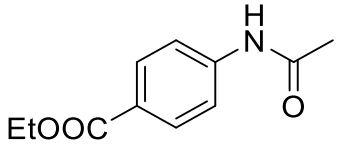
N-(2,5-Dimethylphenyl)acetamide (**4m**)[14]: yield 79%, white solid, m.p. 139.2-140.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (s, 1H), 7.17 (s, 1H), 7.02 (d, J = 7.6 Hz, 1H), 6.84 (d, J = 7.5 Hz, 1H), 2.20 (s, 3H), 2.10 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.1, 136.3, 134.8, 130.0, 128.4, 125.65, 125.56, 23.3, 20.6, 17.5.



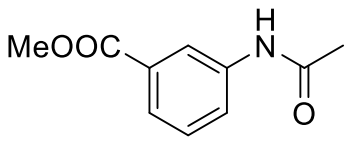
N-(4-Ethylphenyl)acetamide (**4n**)[15]: yield 79%, white solid, m.p. 85.8-86.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.81 (s, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 2.51 (q, J = 7.6 Hz, 2H), 1.99 (s, 3H), 1.12 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.0, 138.3, 137.1, 127.9, 119.1, 27.6, 24.0, 15.8.



Methyl 4-acetamidobenzoate (**4o**)[16]: yield 80%, white solid, m.p. 113.5-114.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.22 (s, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9, 165.8, 143.7, 130.3, 123.7, 118.3, 51.8, 24.2.

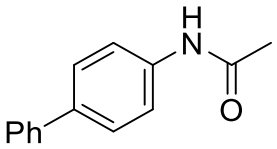


Ethyl 4-acetamidobenzoate (**4p**)[17]: yield 81%, white solid, m.p. 179.3-180.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.26 (s, 1H), 7.87 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 2.05 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.0, 165.9, 143.74, 130.3, 123.7, 118.3, 51.9, 24.2, 10.0.

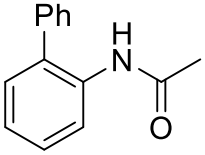


Methyl 3-acetamidobenzoate (**4q**)[18]: yield 82%, white solid, m.p. 131.7-132.6 °C; ^{1}H NMR (400

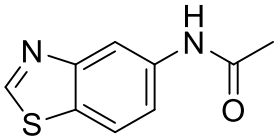
MHz, DMSO-d_6) δ ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.13 (s, 1H), 8.21 (s, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 3.81 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.7, 166.2, 139.7, 130.1, 128.2, 123.6, 123.4, 119.4, 52.2, 24.0.



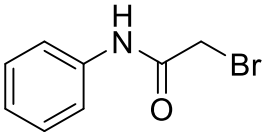
N-([1,1'-Biphenyl]-4-yl)acetamide (**4r**)[19]: yield 58%, white solid, m.p. 169.3-169.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.98 (s, 1H), 7.64 (d, J = 8.5 Hz, 2H), 7.56 (t, J = 8.0 Hz, 4H), 7.37 (t, J = 7.6 Hz, 2H), 7.25 (t, J = 7.3 Hz, 1H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.3, 139.8, 138.8, 134.6, 128.9, 126.9, 126.9, 126.2, 119.3, 24.0.



N-([1,1'-Biphenyl]-2-yl)acetamide (**4s**)[20]: yield 55%, white solid, m.p. 119.4-120.1 °C; ^{1}H NMR (101 MHz, DMSO-d_6) δ 9.22 (s, 1H), 7.48-7.20 (m, 9H), 1.87 (s, 3H); ^{13}C NMR (400 MHz, DMSO-d_6) δ 168.7, 139.0, 136.7, 134.9, 130.2, 128.7, 128.4, 127.6, 127.4, 127.2, 126.0, 23.0.



N-(Benzo[d]thiazol-5-yl)acetamide (**4t**)[21]: yield 73%, white solid, m.p. 192.0-192.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.08 (s, 1H), 9.25 (s, 1H), 8.40 (d, J = 1.8 Hz, 1H), 7.93 (d, J = 8.7 Hz, 1H), 7.50 (dd, J = 8.7, 1.9 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.6, 156.8, 153.6, 138.0, 127.7, 122.2, 117.9, 112.6, 24.1.



2-Bromo-*N*-phenylacetamide(**4u**)[22]: yield 59%, white solid, m.p. 127.4-128.0 °C; ^{1}H NMR (400 MHz, DMSO) δ 10.34 (s, 1H), 7.54 (d, J = 7.9 Hz, 2H), 7.28 (t, J = 7.9 Hz, 2H), 7.03 (t, J = 7.4 Hz, 1H), 3.99 (s, 2H); ^{13}C NMR (400 MHz, DMSO) δ 164.8, 138.6, 128.9, 123.9, 119.2, 30.5.

4. References

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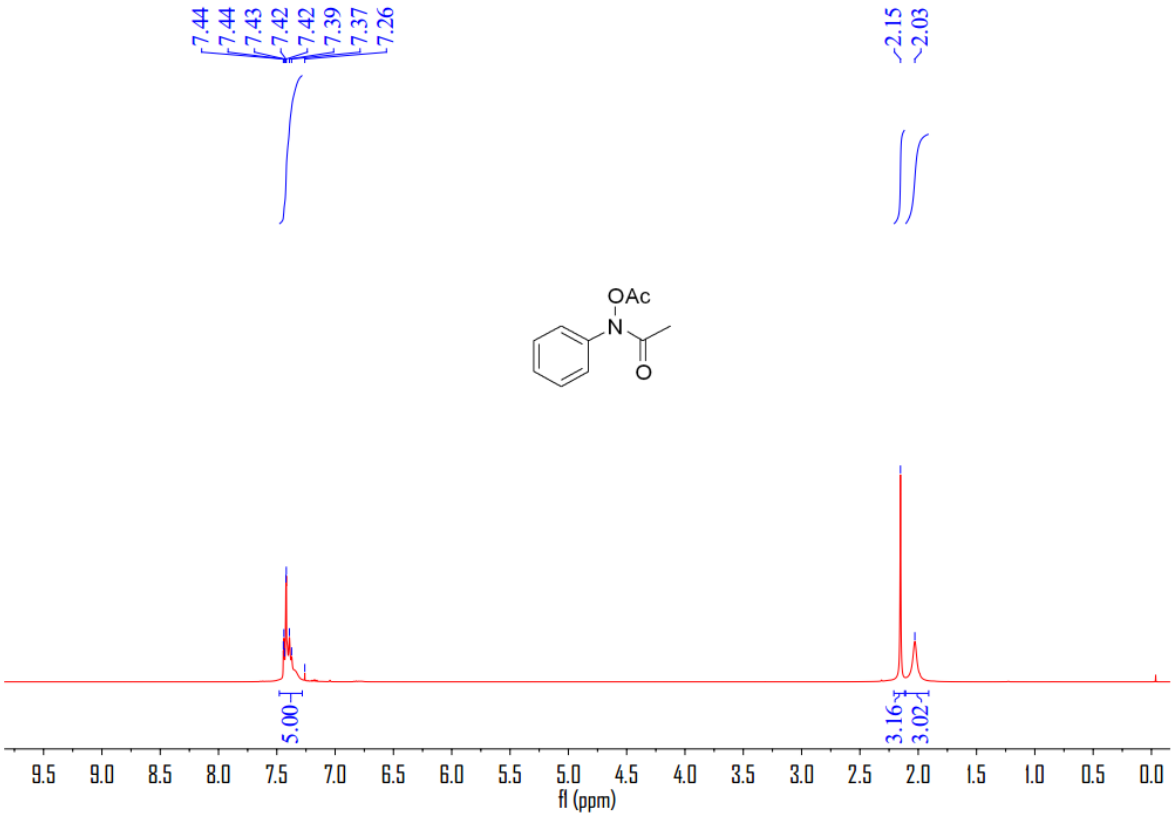
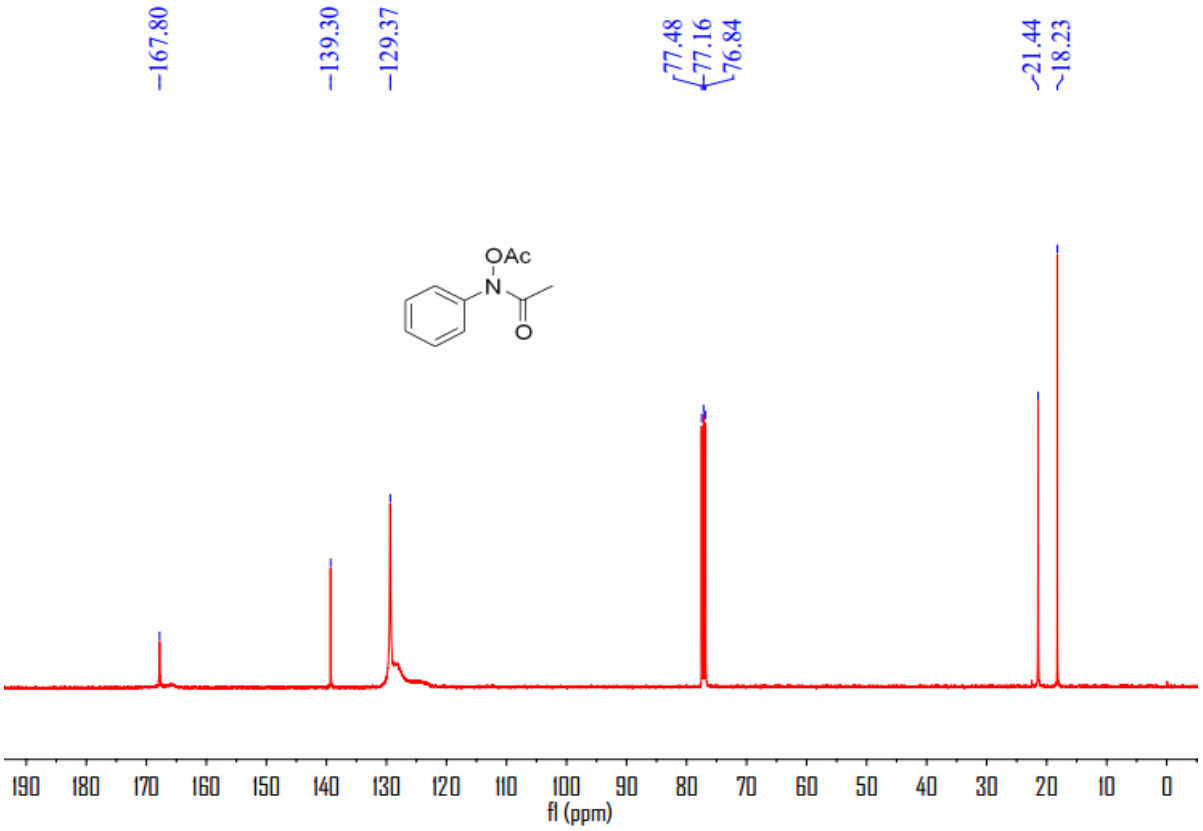
5. NMR Spectra

^{1}H NMR of **6a**



^{13}C NMR of **6a**



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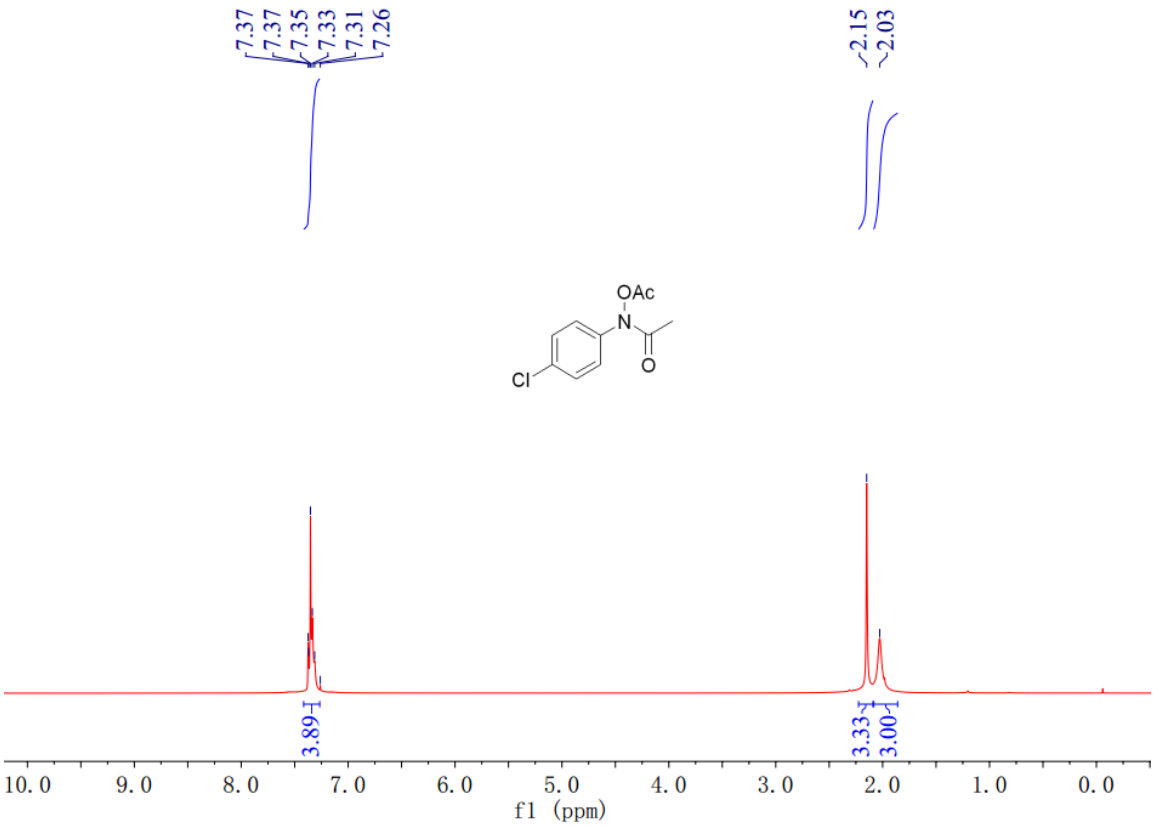

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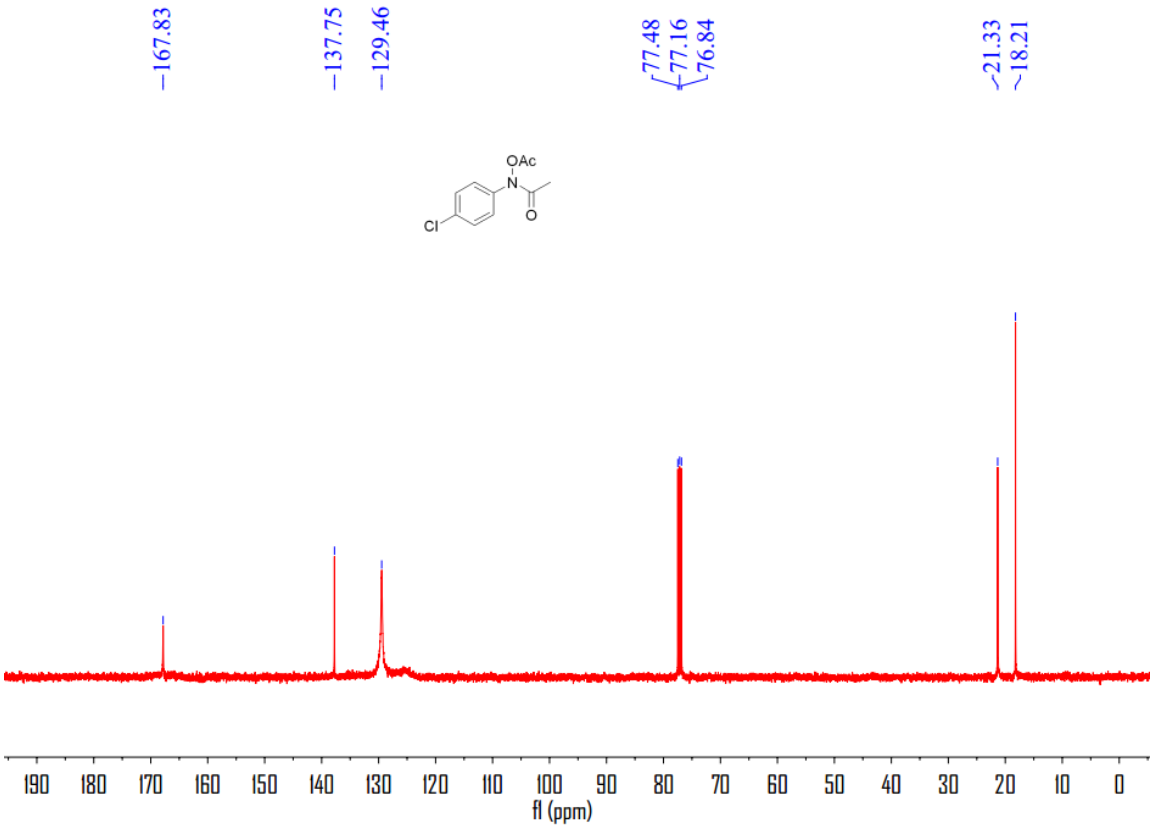
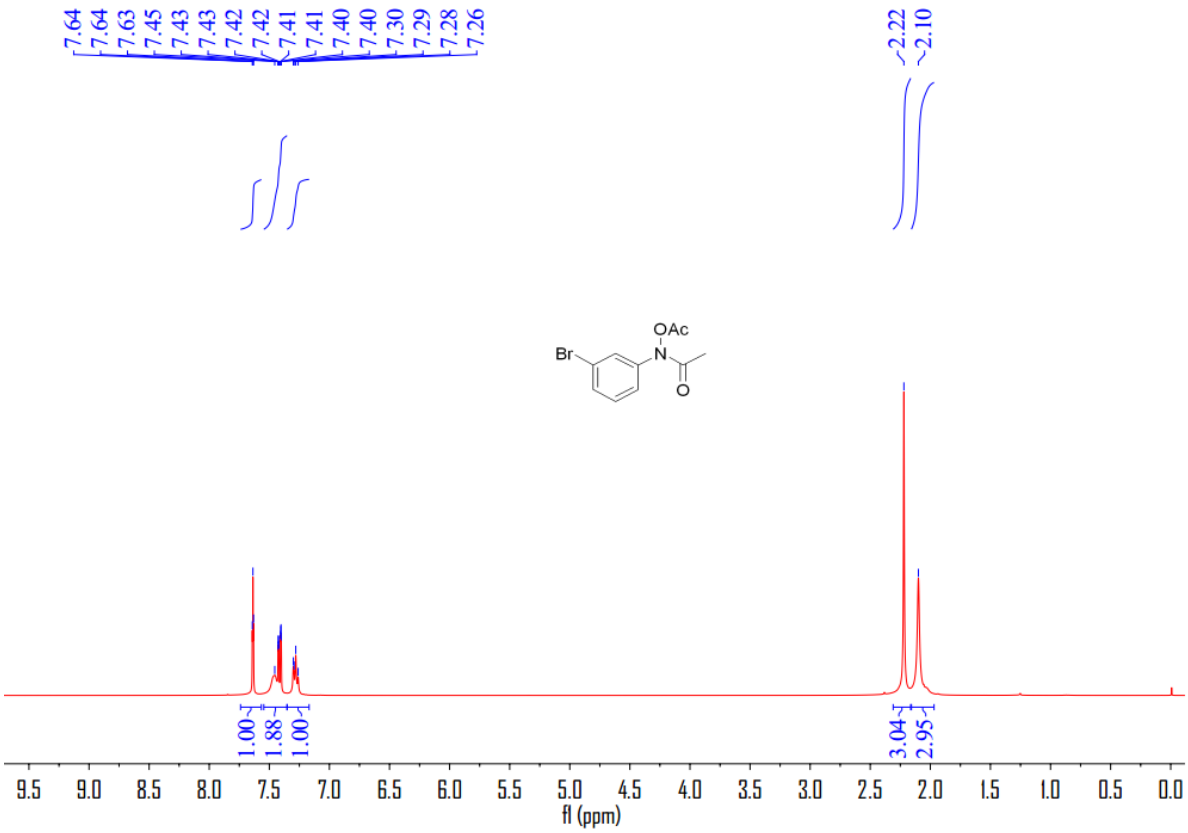
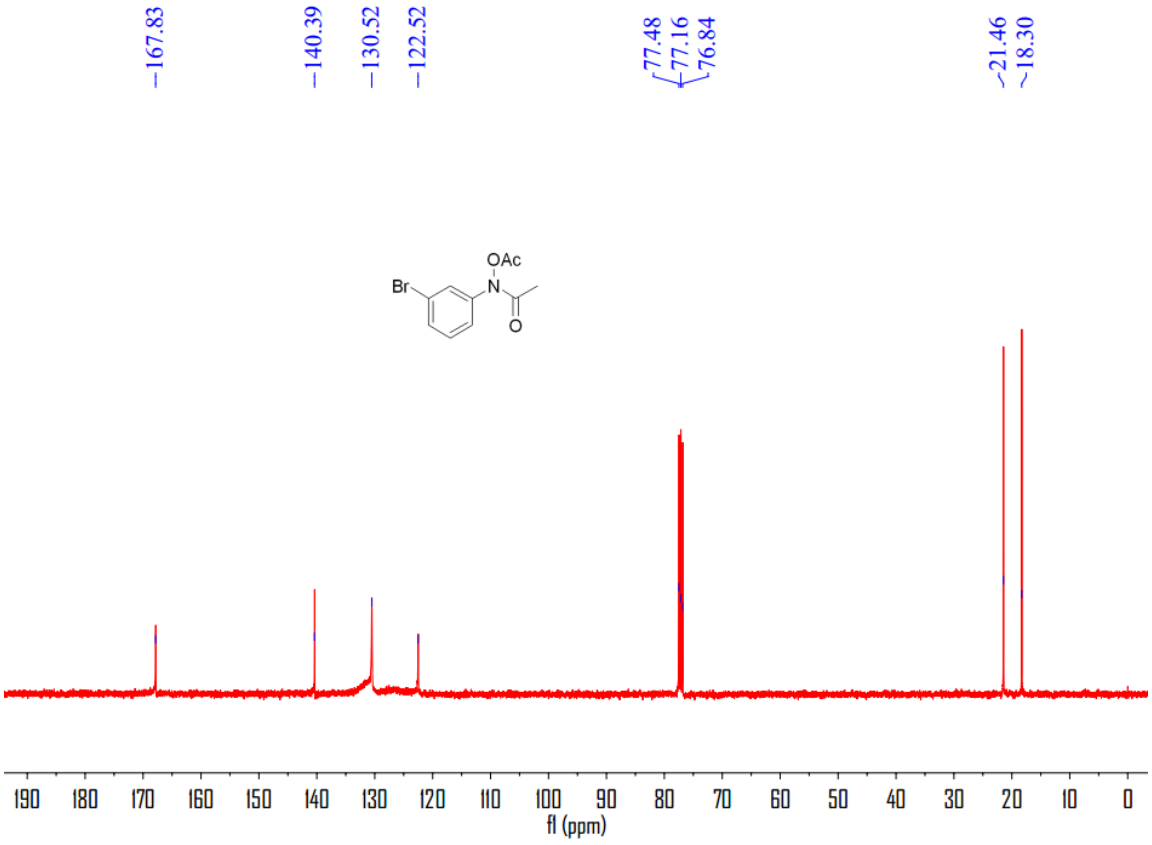


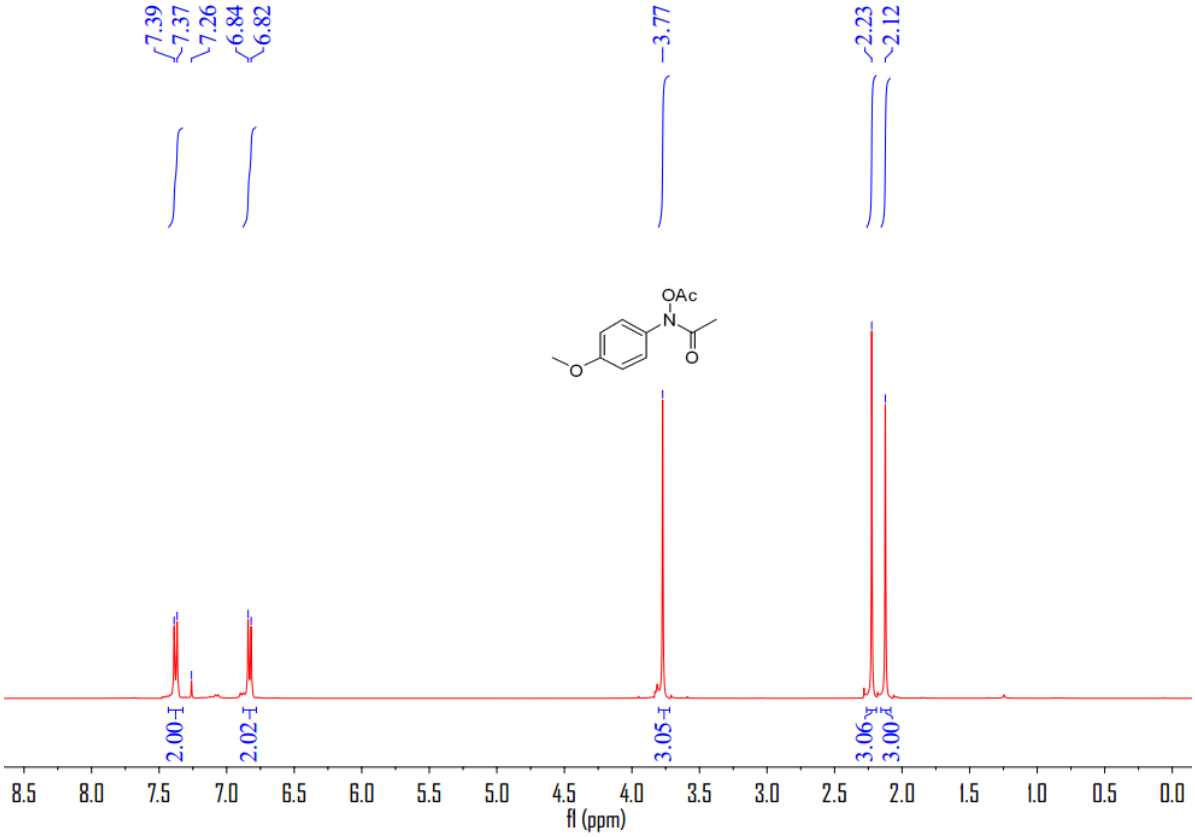
^{1}H NMR of **6c**



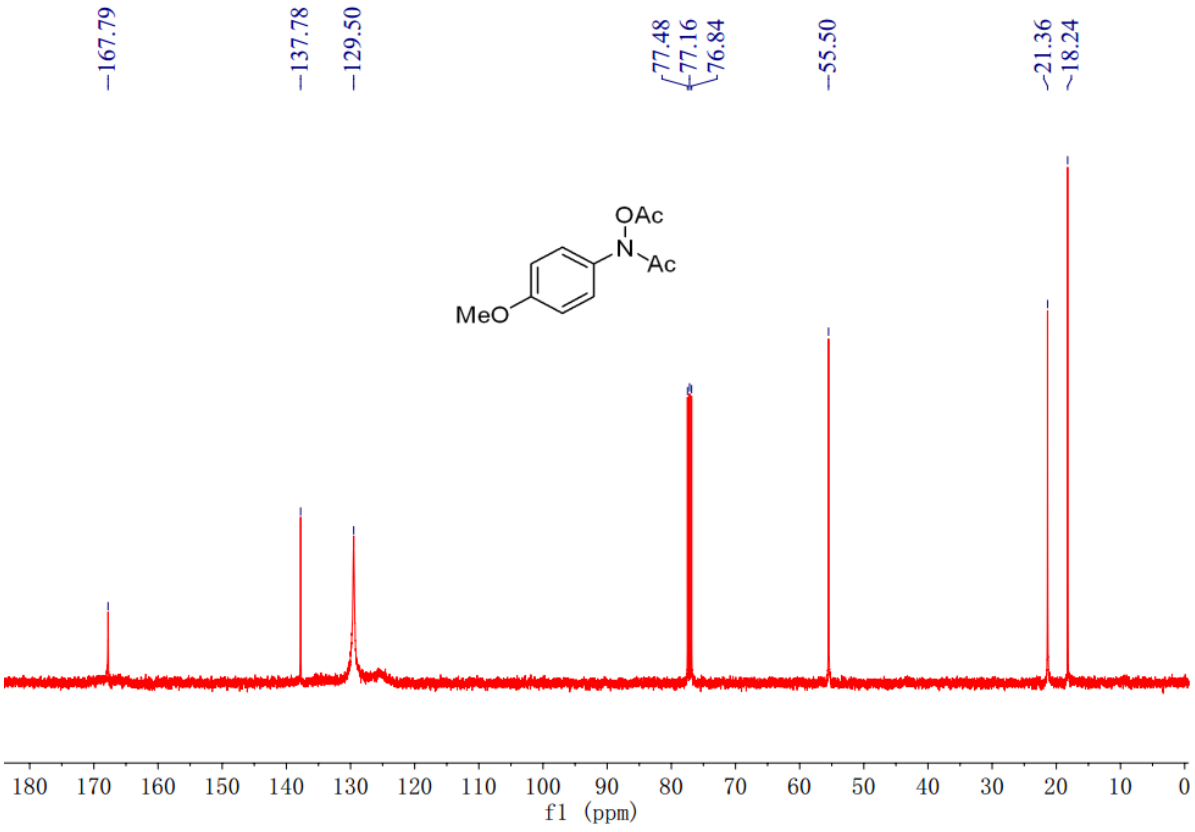
^{13}C NMR of **6c**



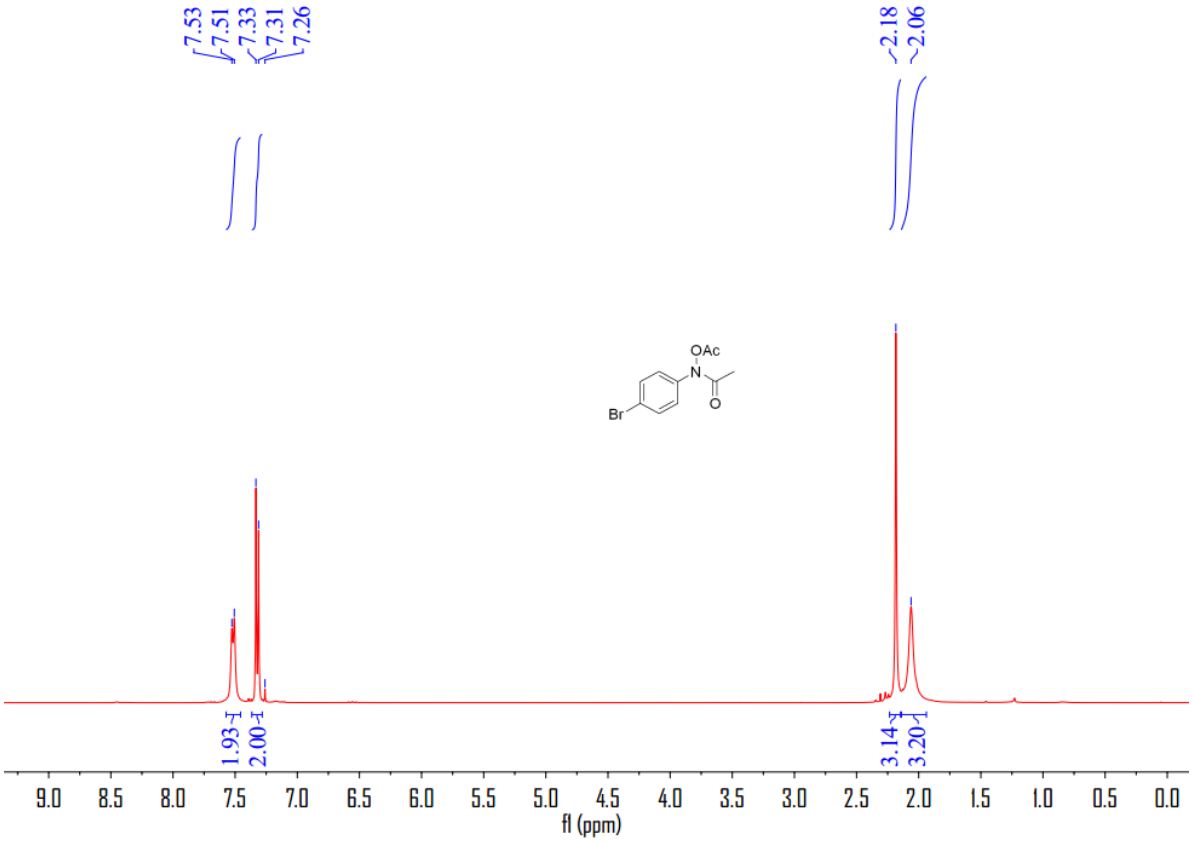
^{1}H NMR of **6d**



^{13}C NMR of **6d**



^{1}H NMR of **6e**



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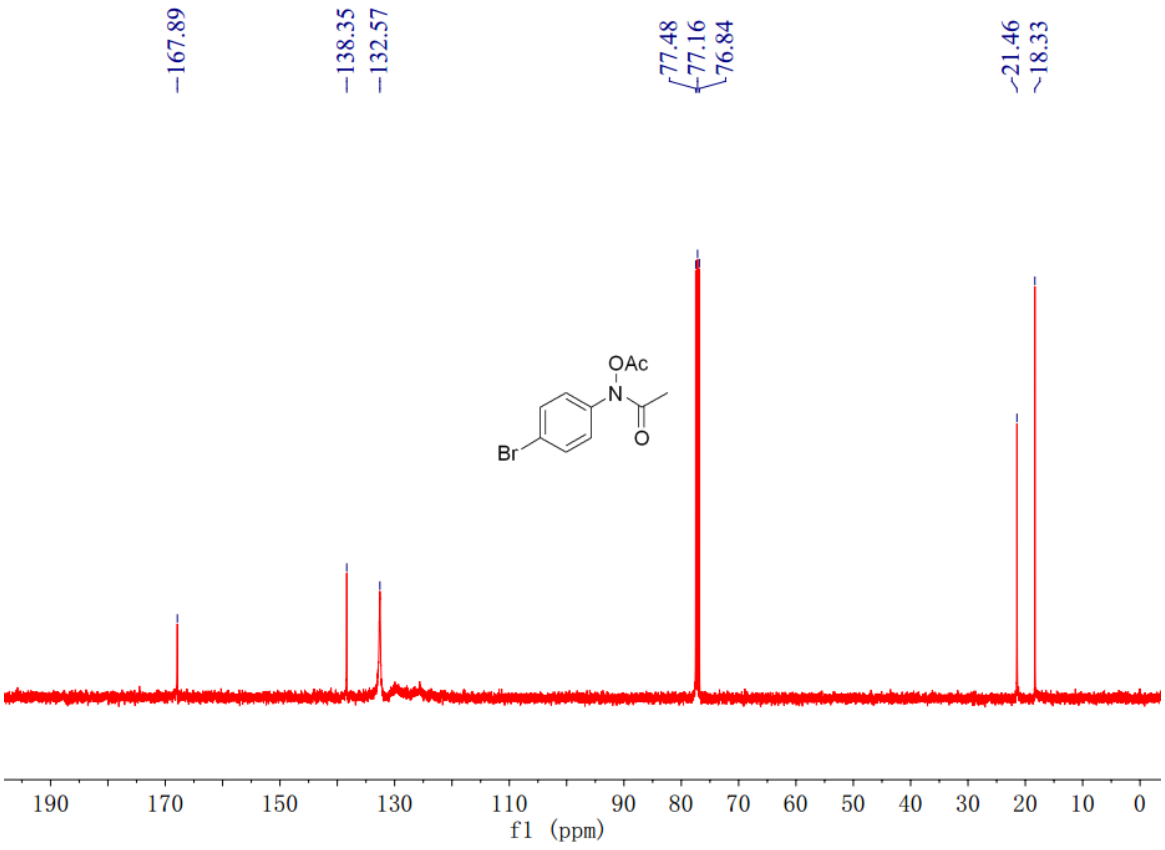
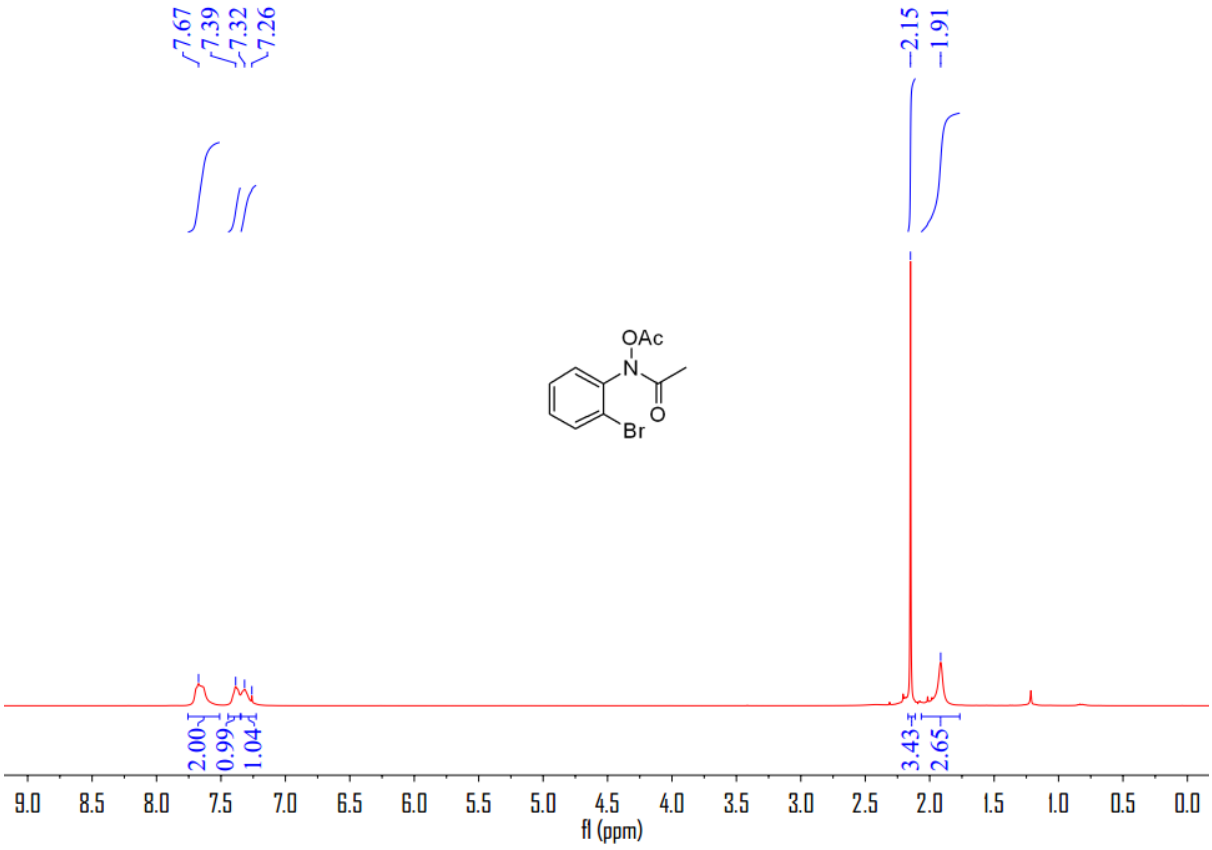


^{1}H NMR of **6f**



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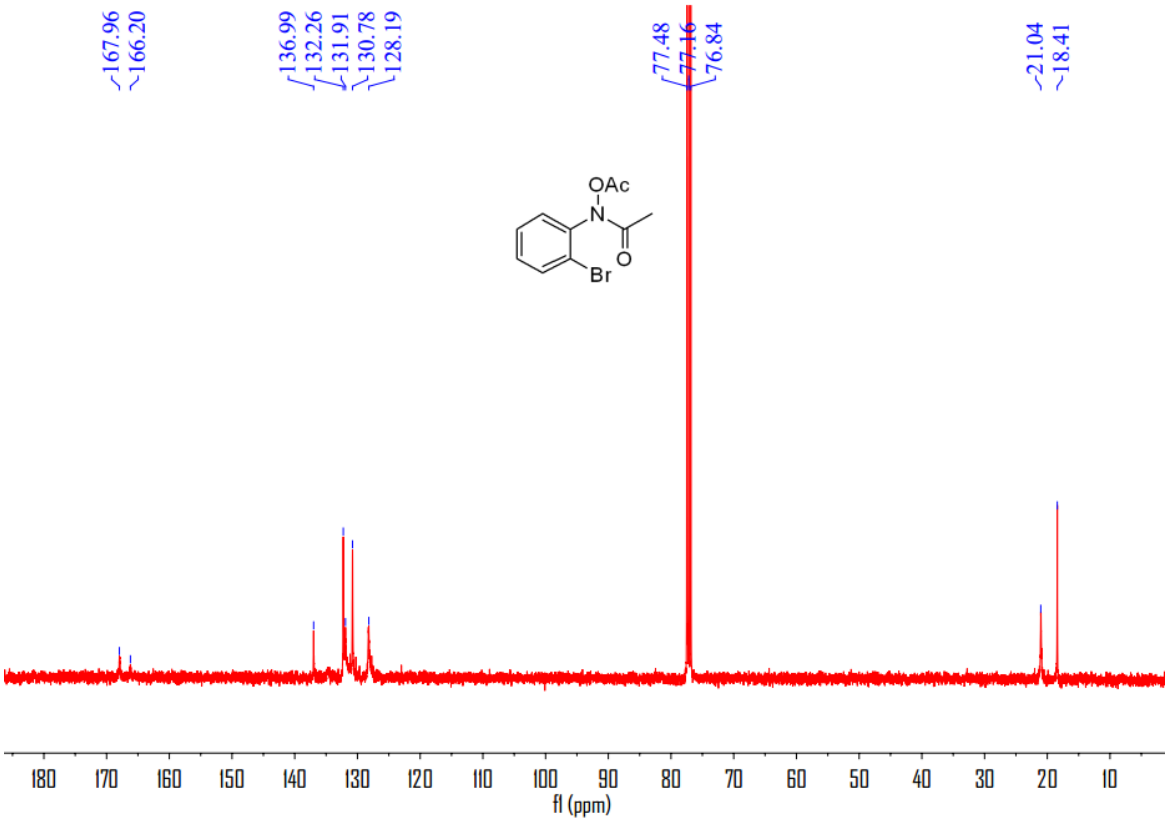

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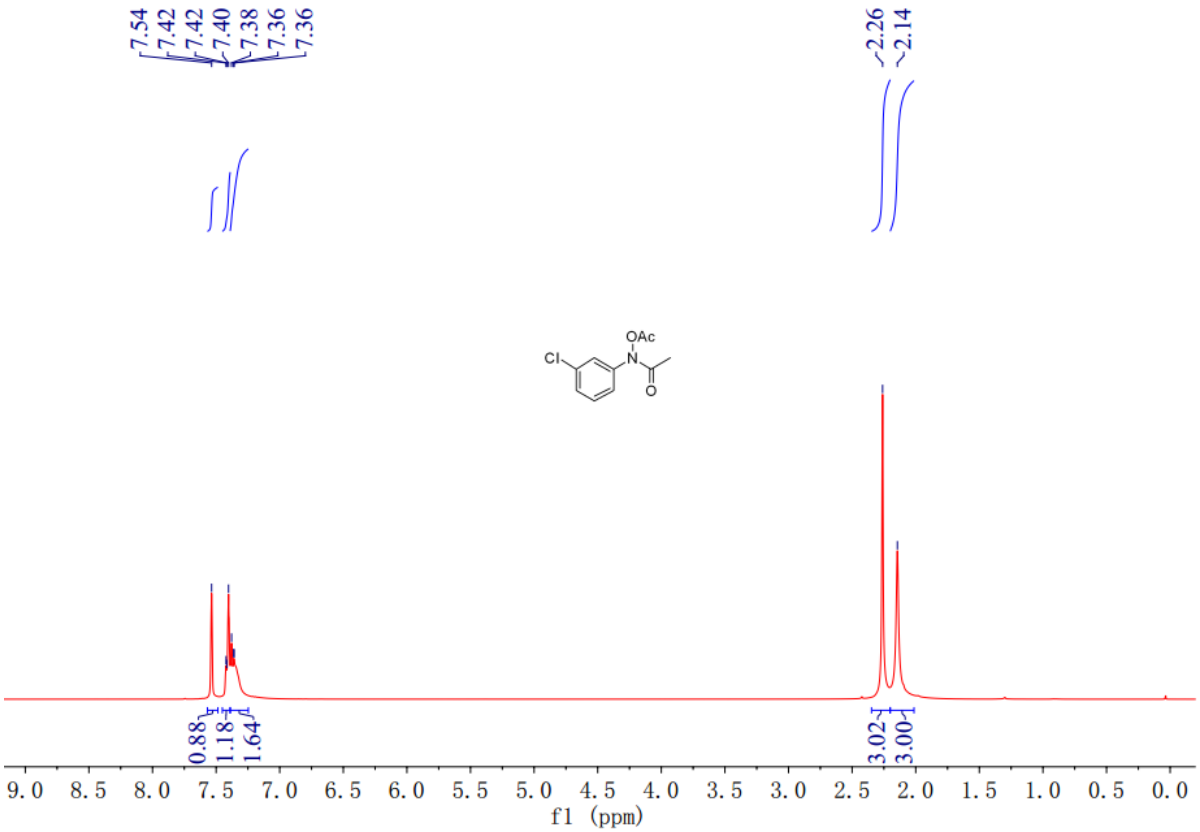

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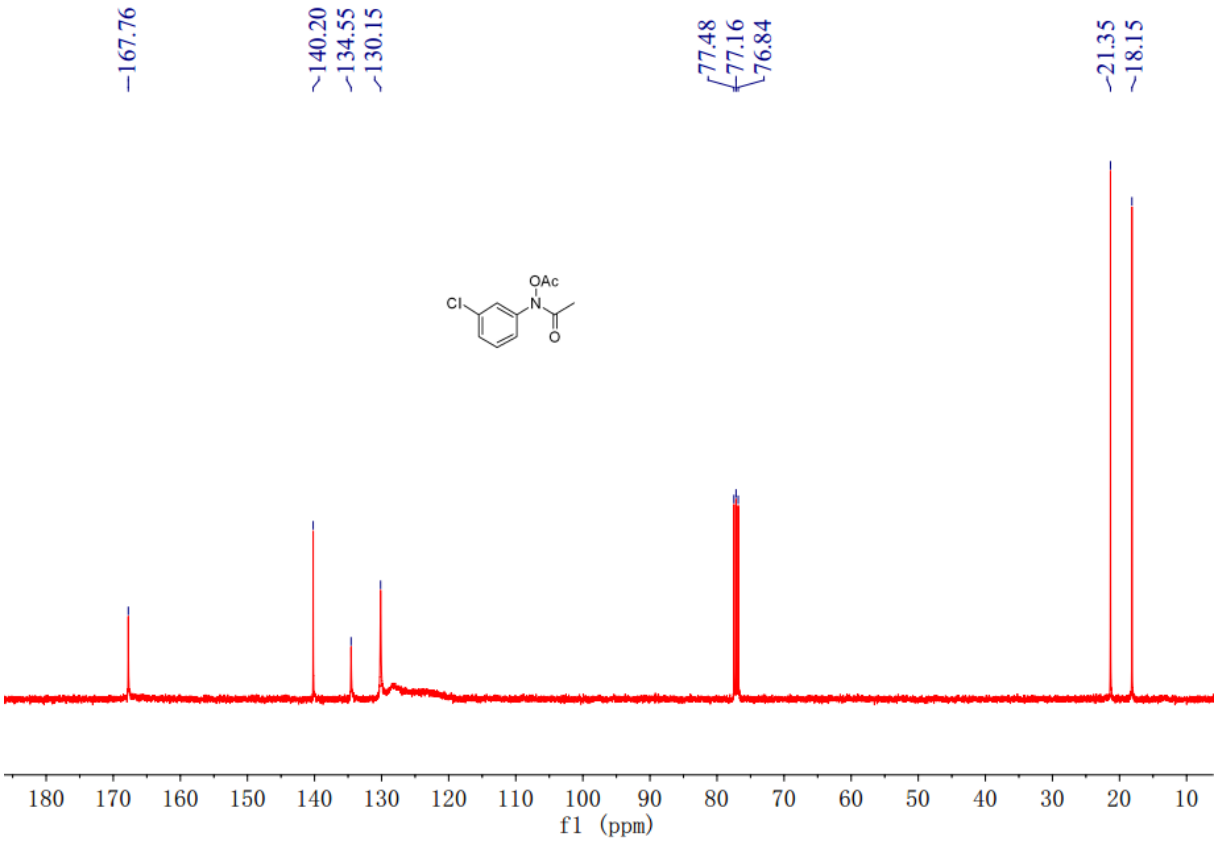

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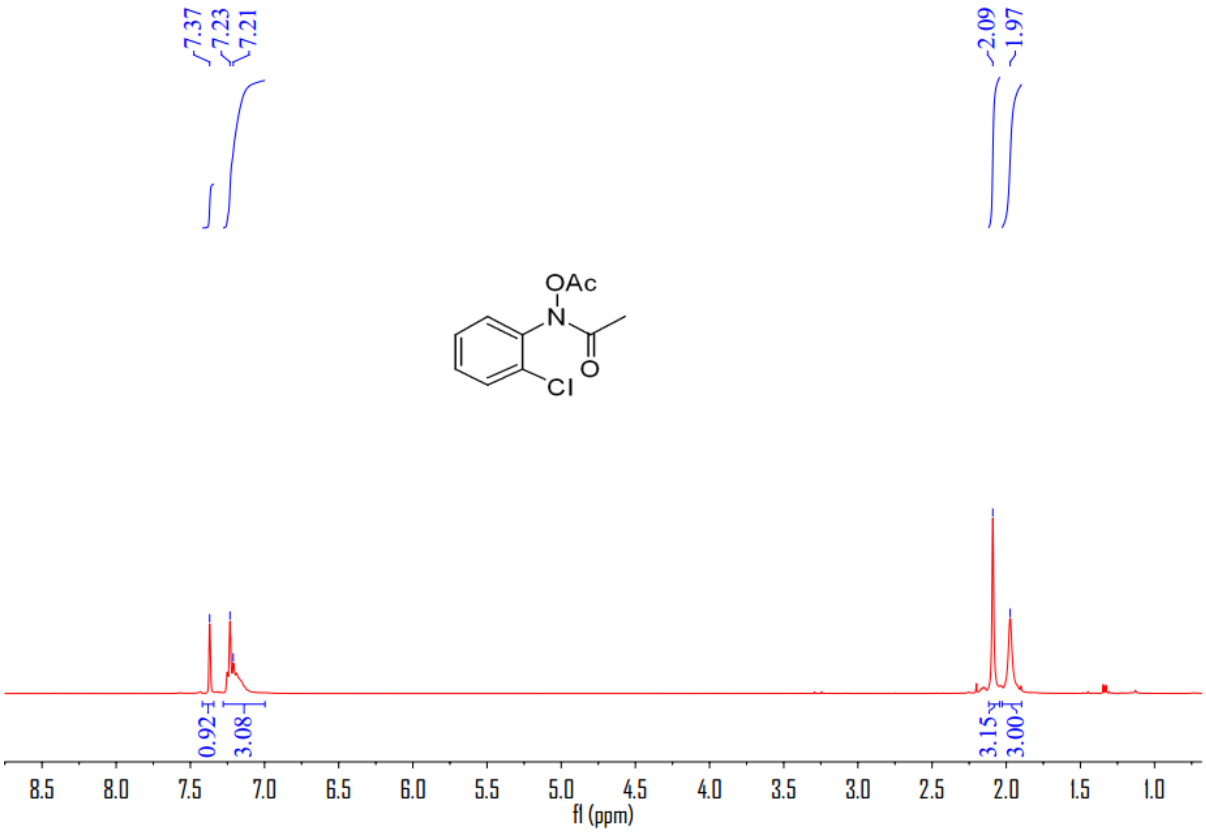

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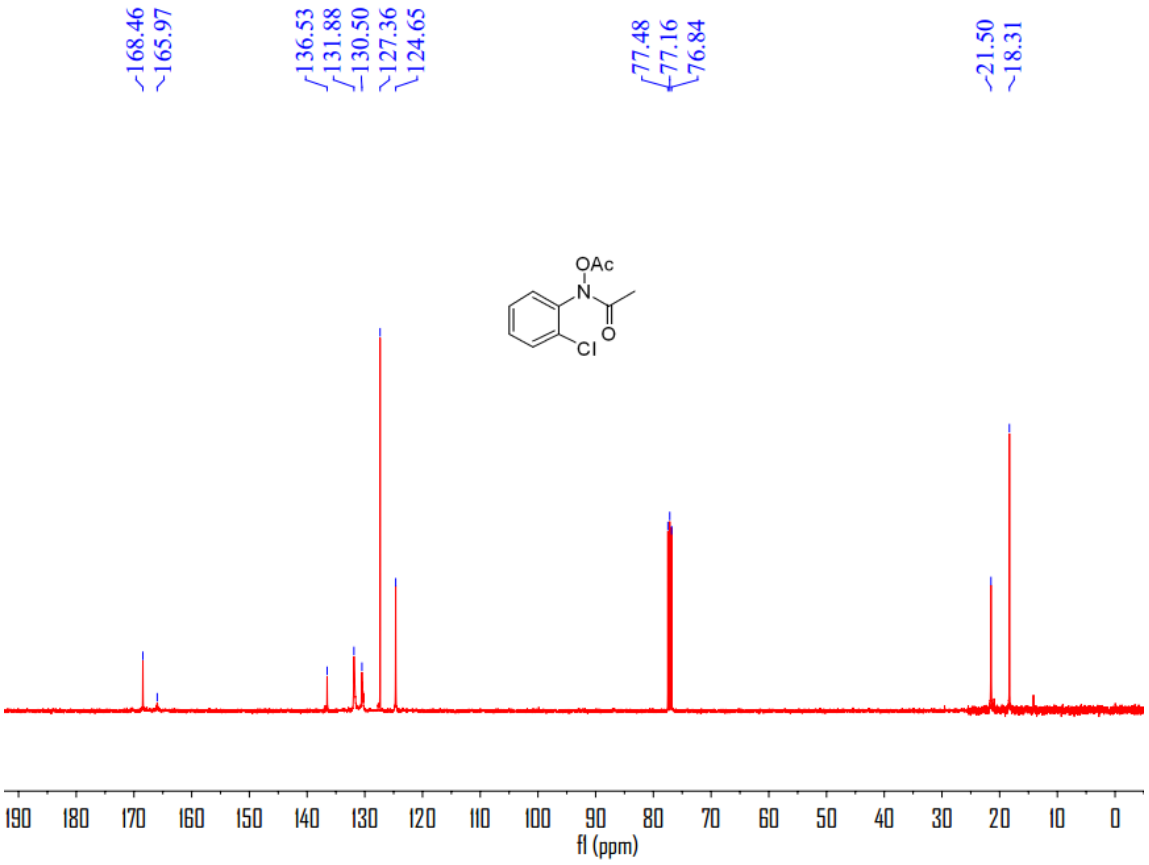
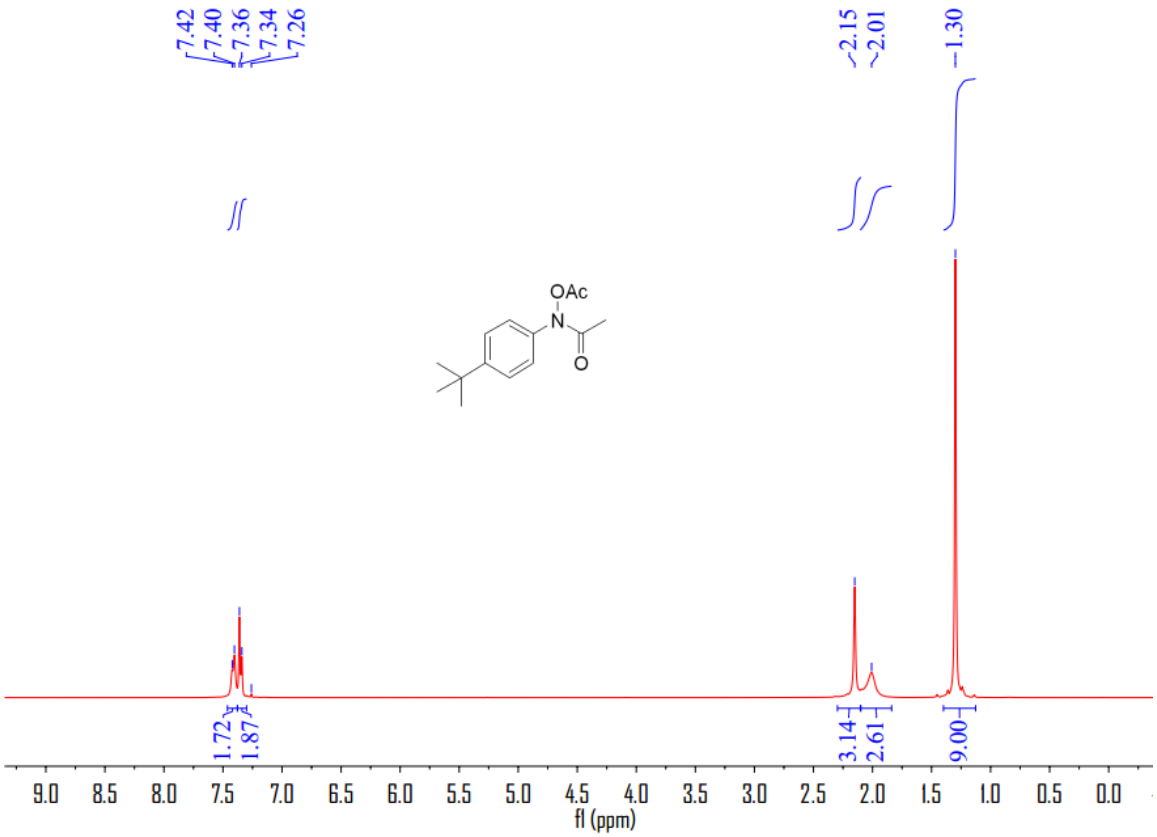
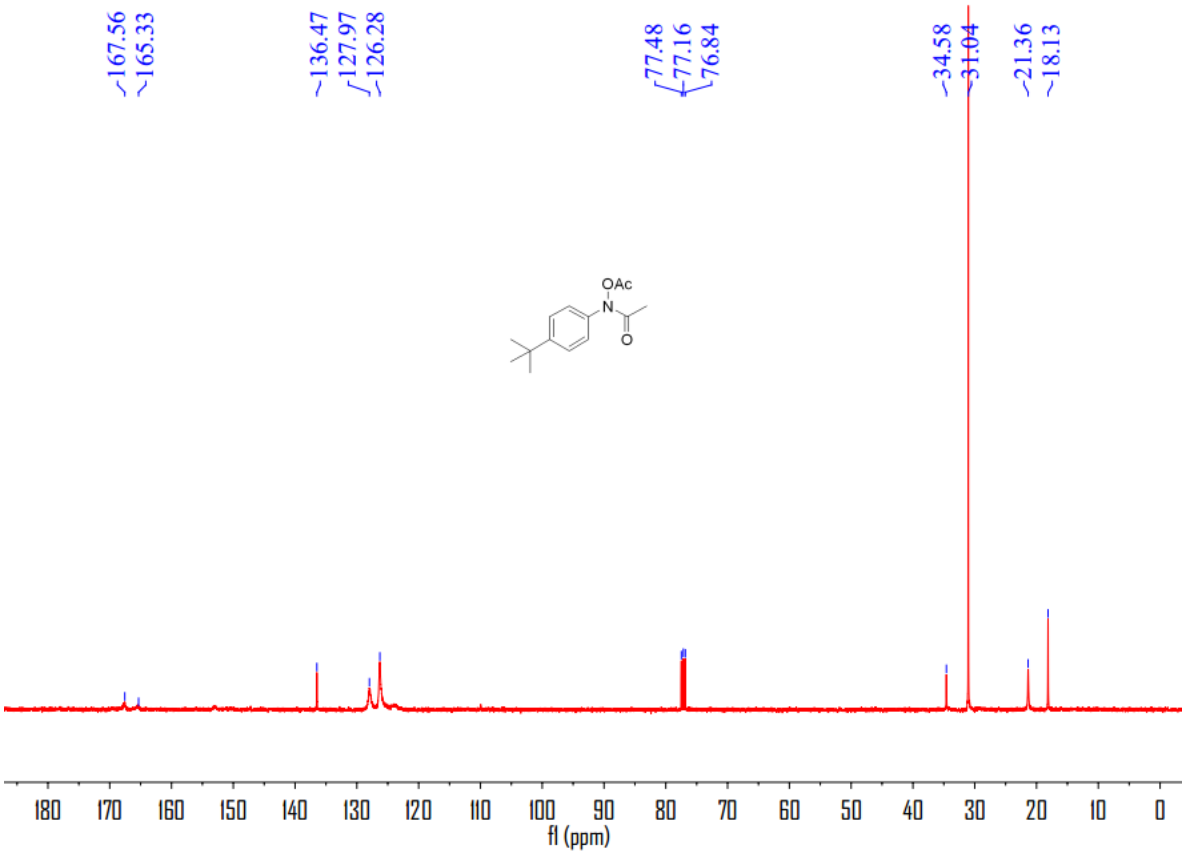


^{1}H NMR of **6i**



^{13}C NMR of **6i**



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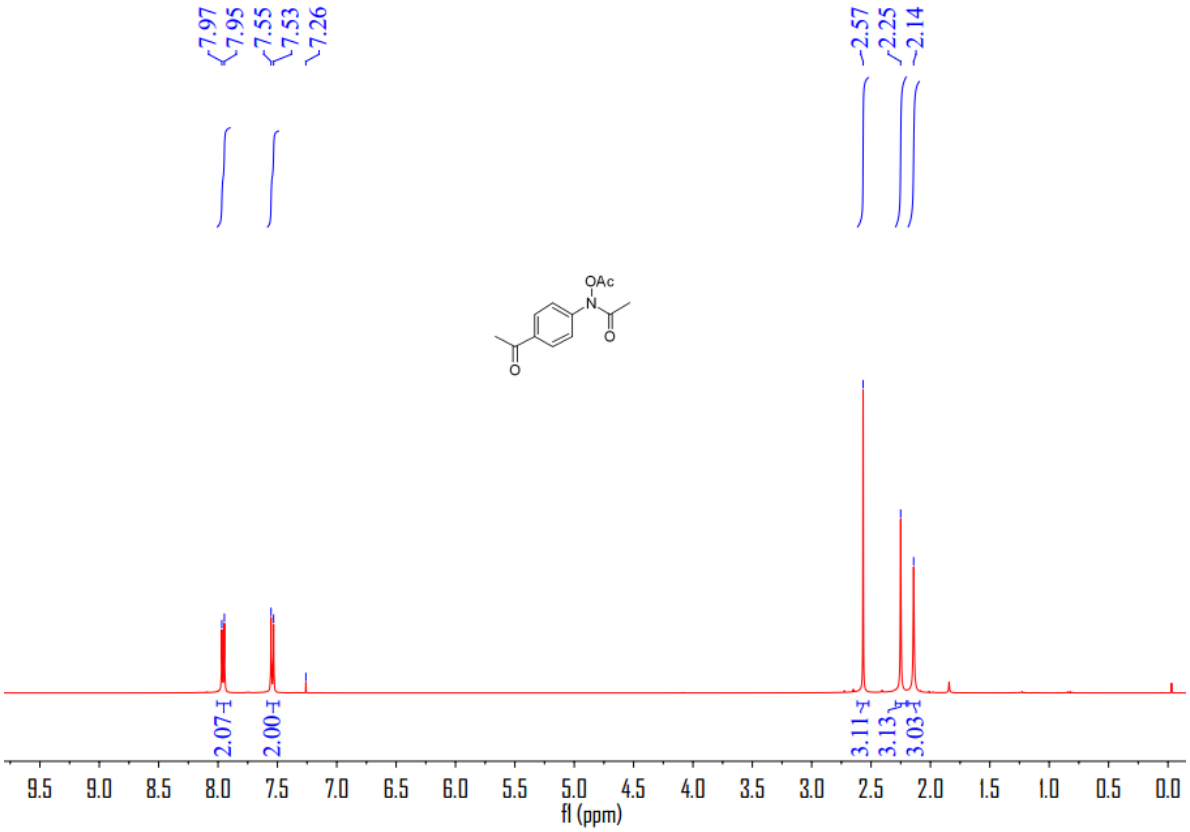

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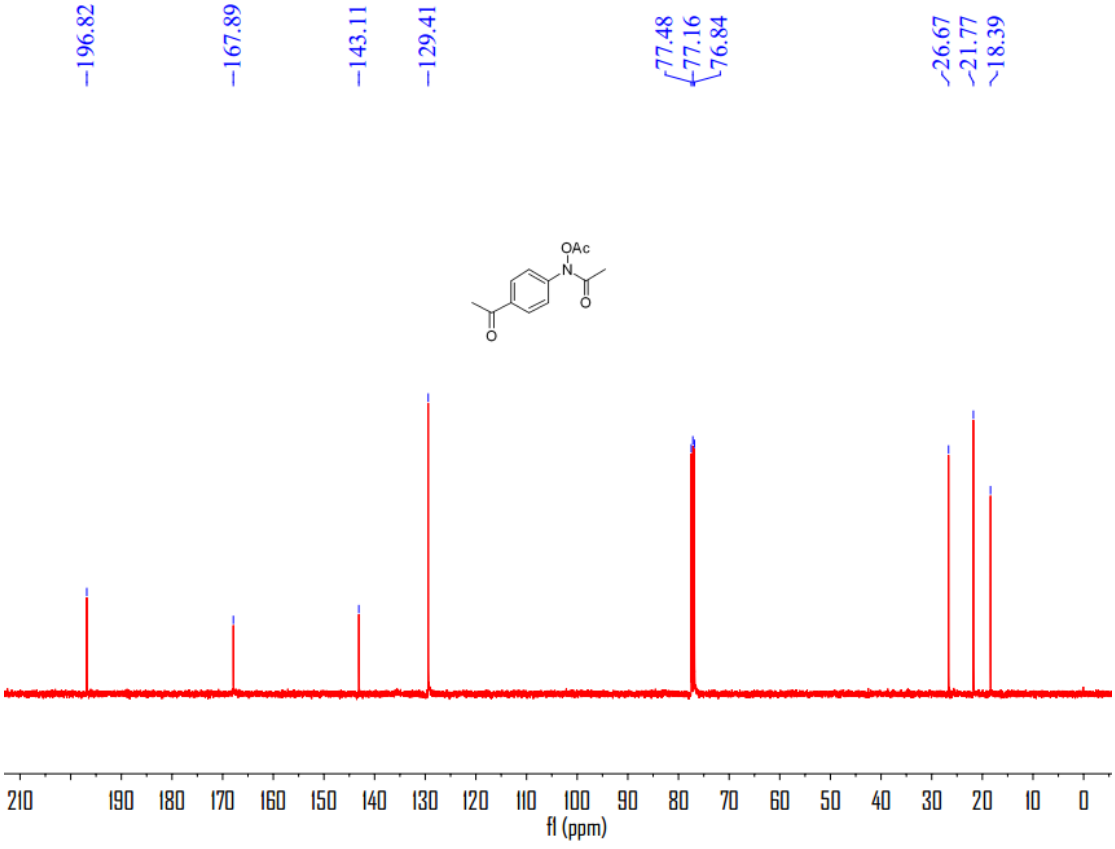

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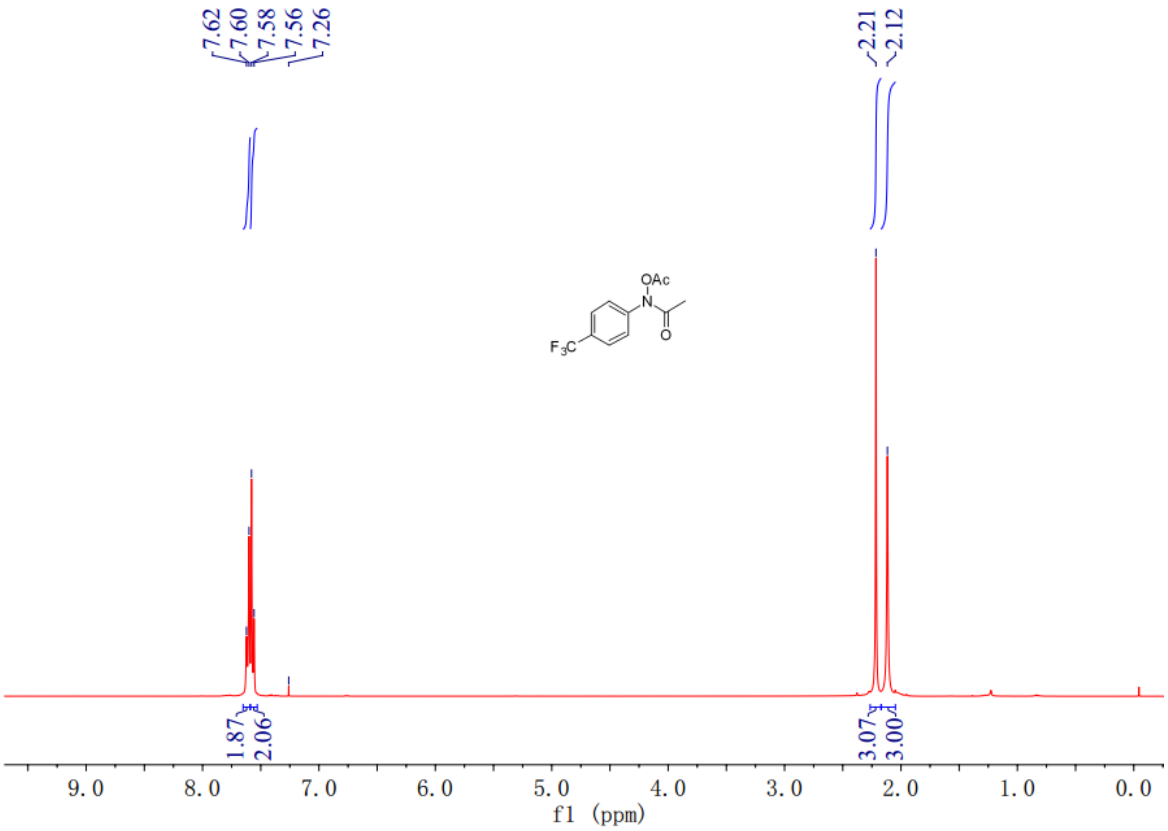

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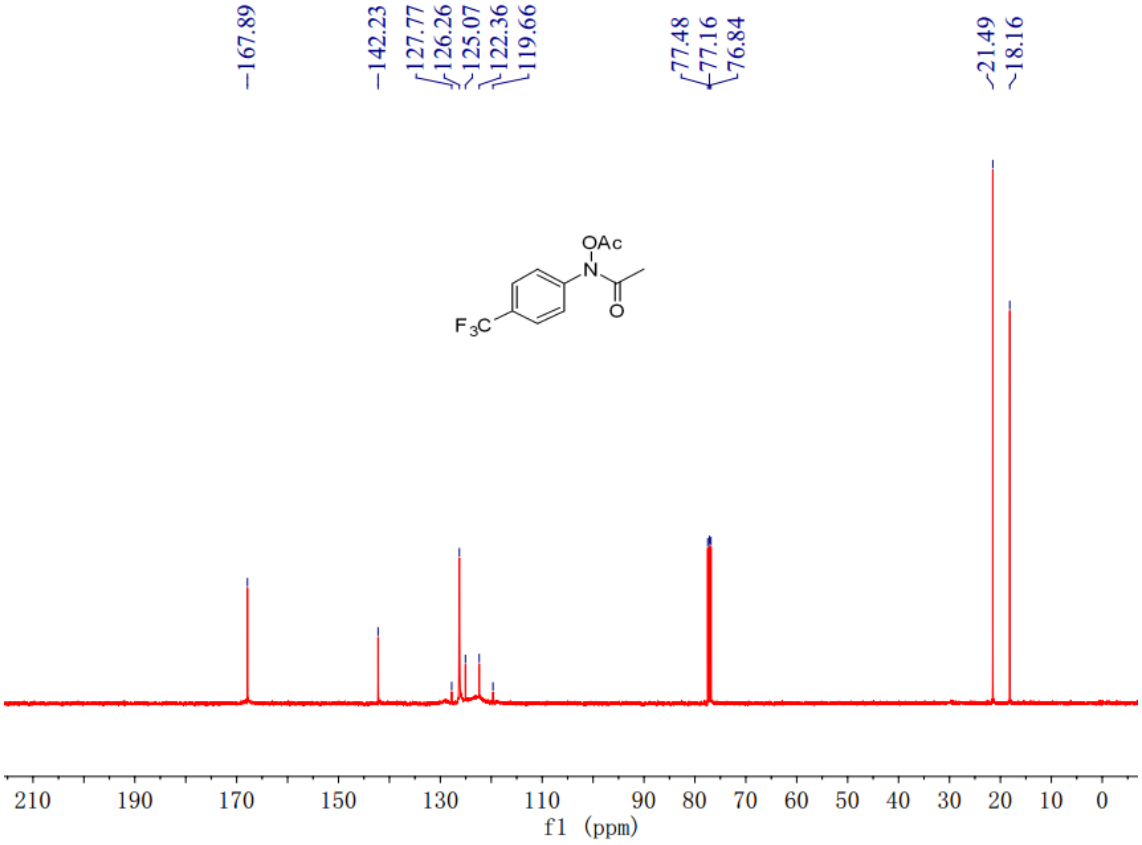
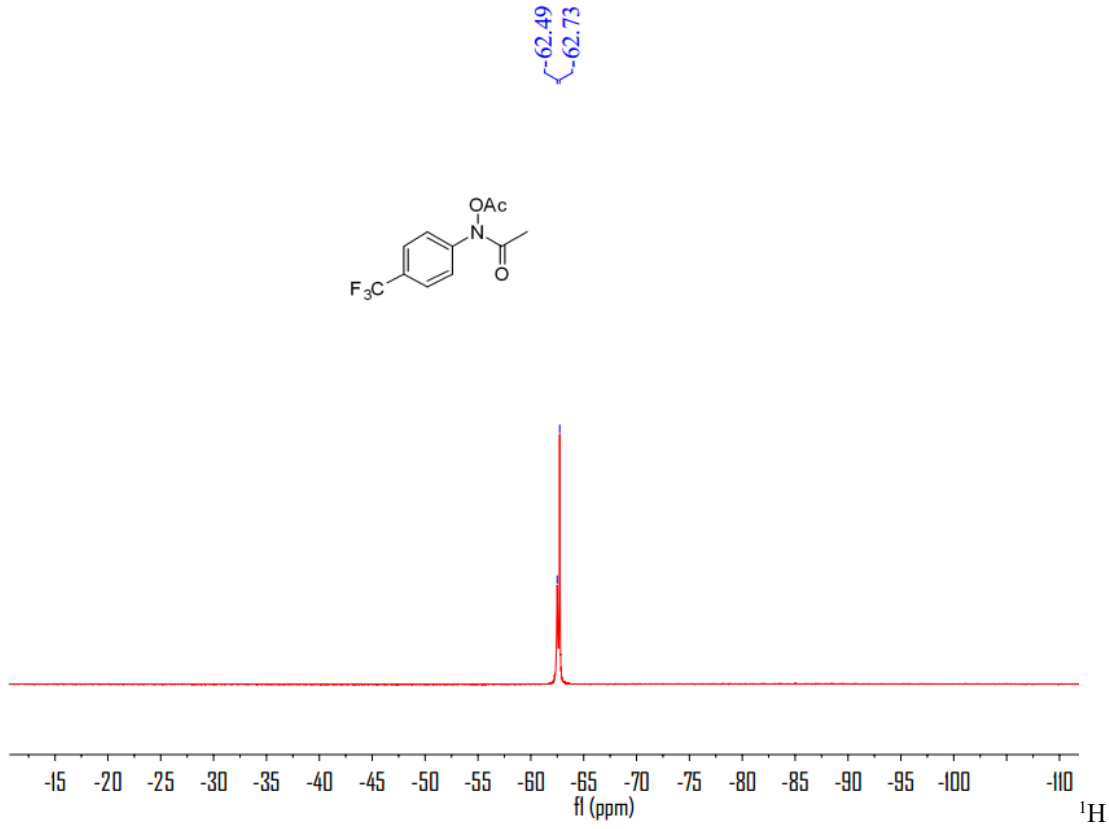
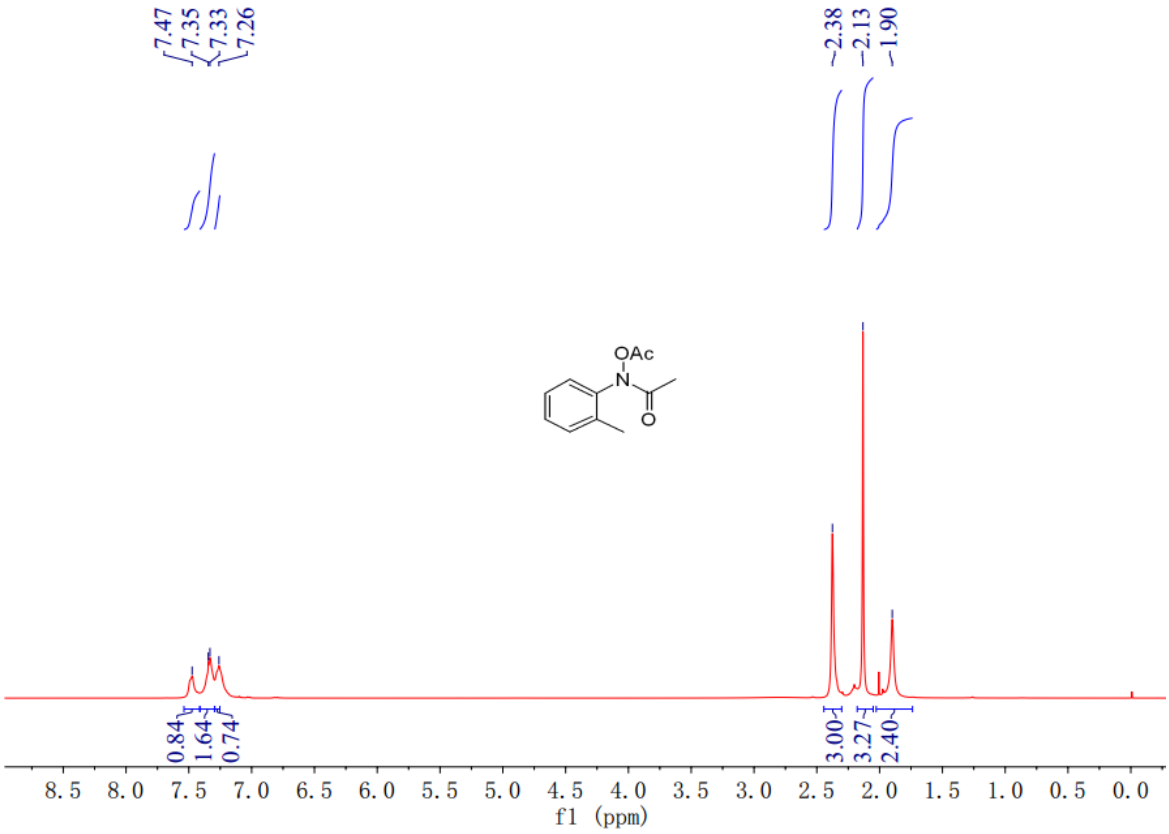


^{19}F NMR of **6k**



^{1}H NMR of **6l**



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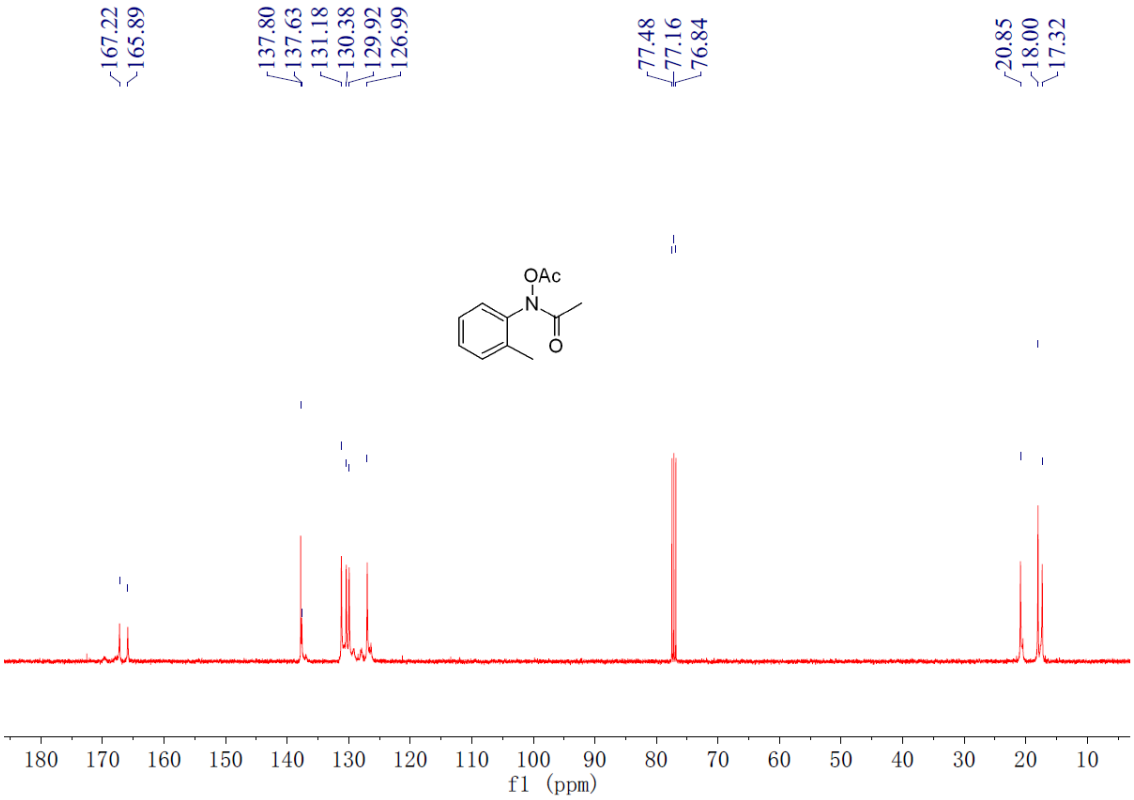

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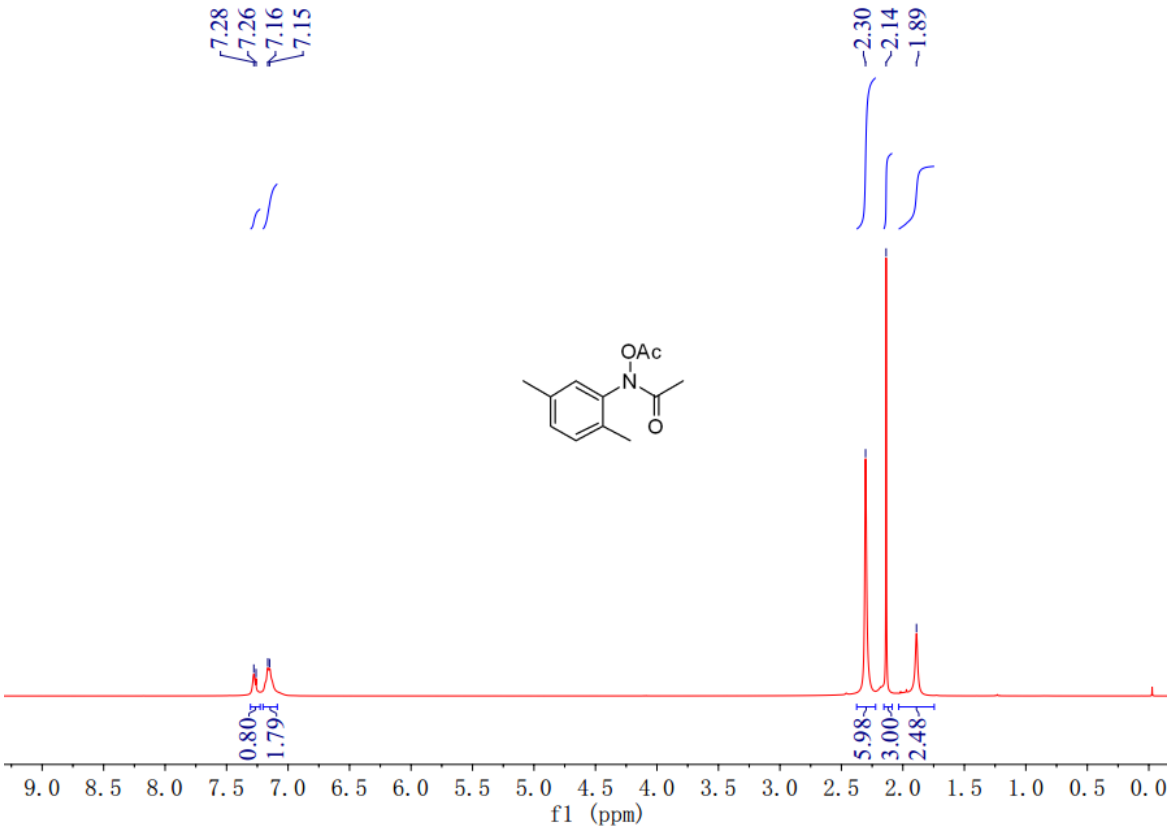

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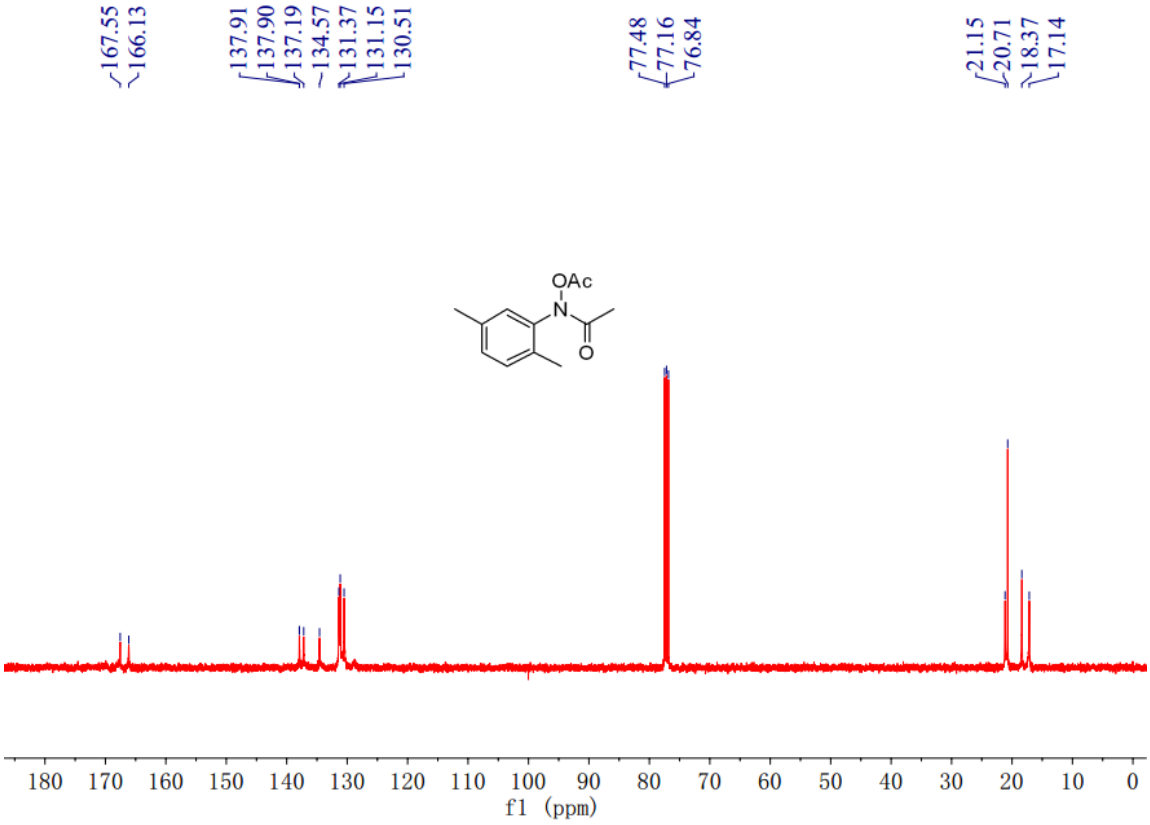

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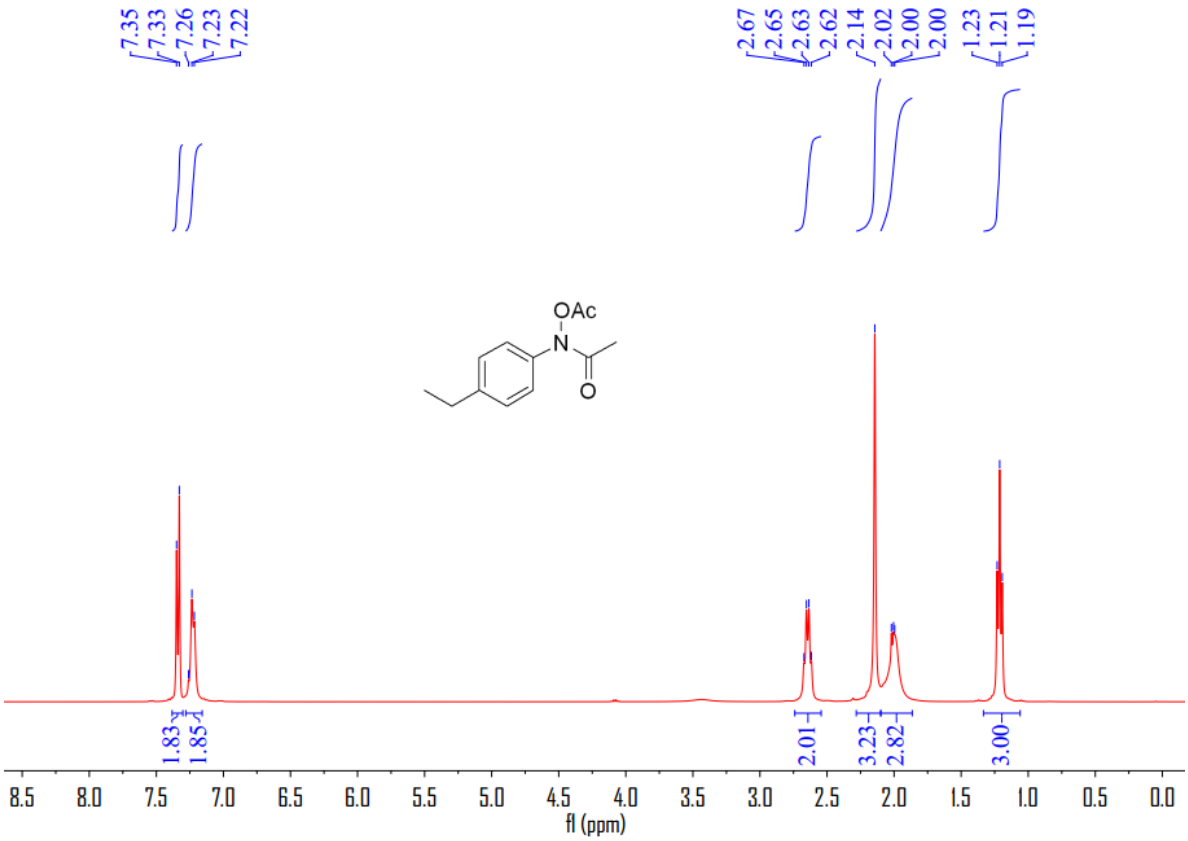

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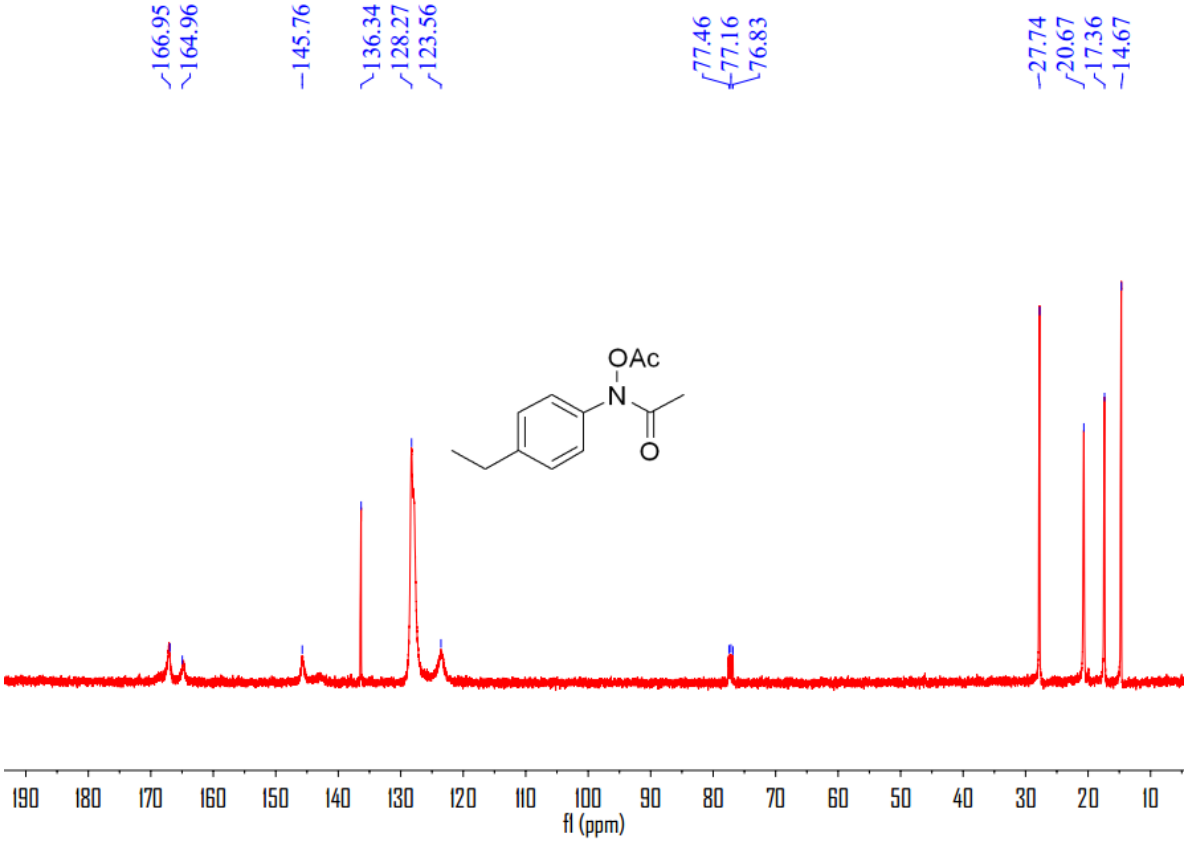

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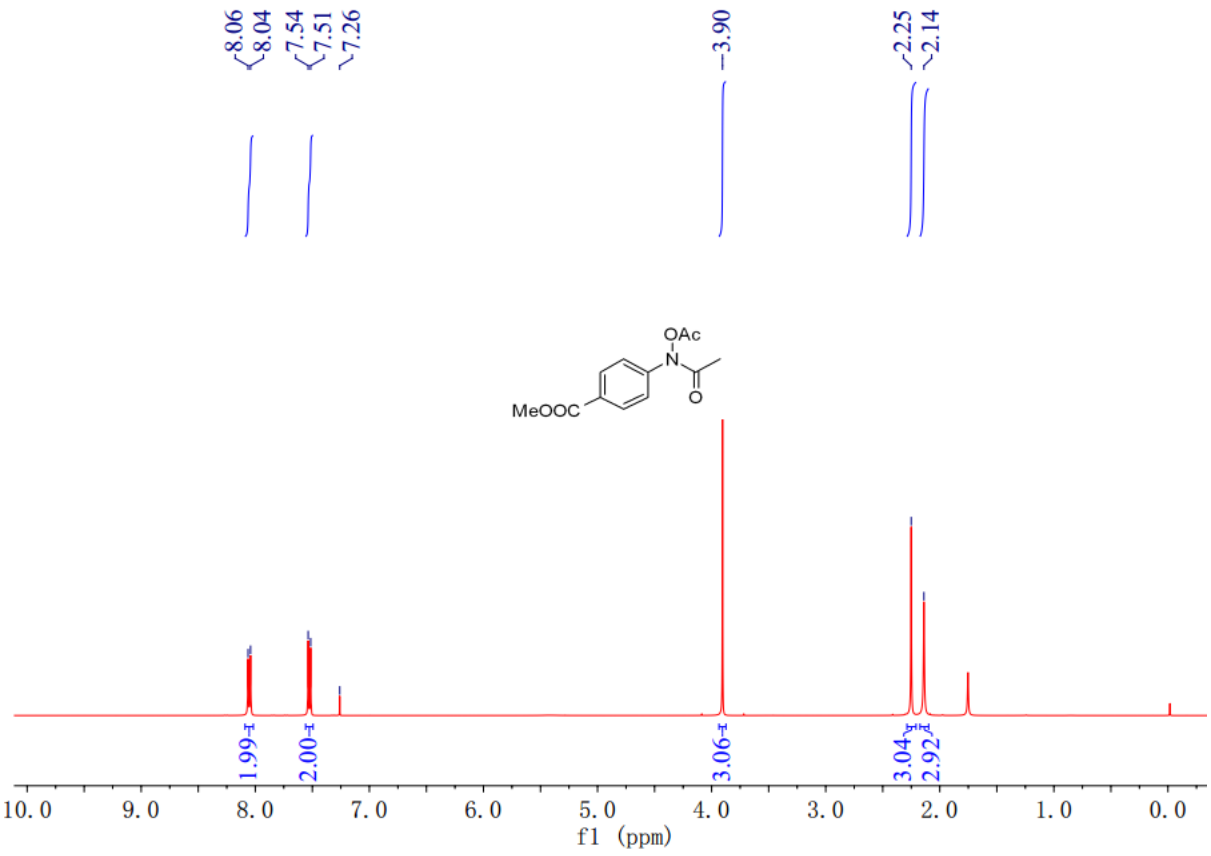

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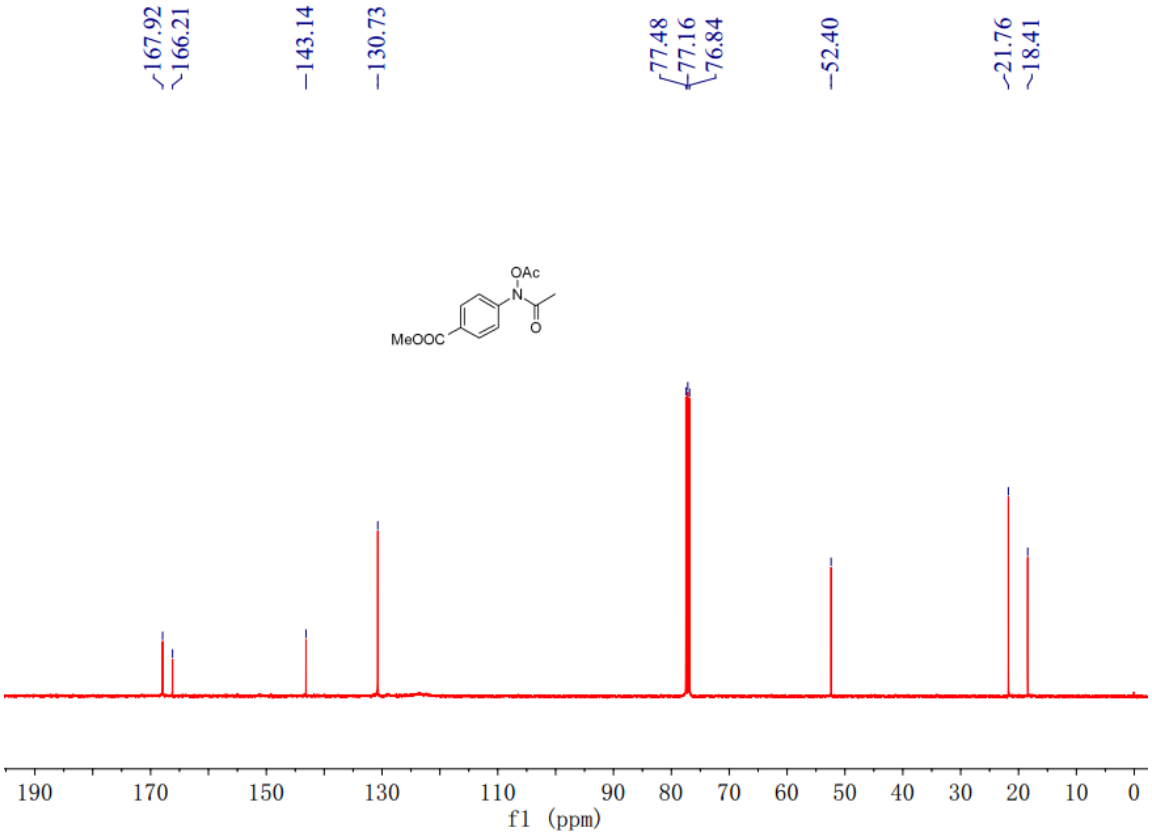

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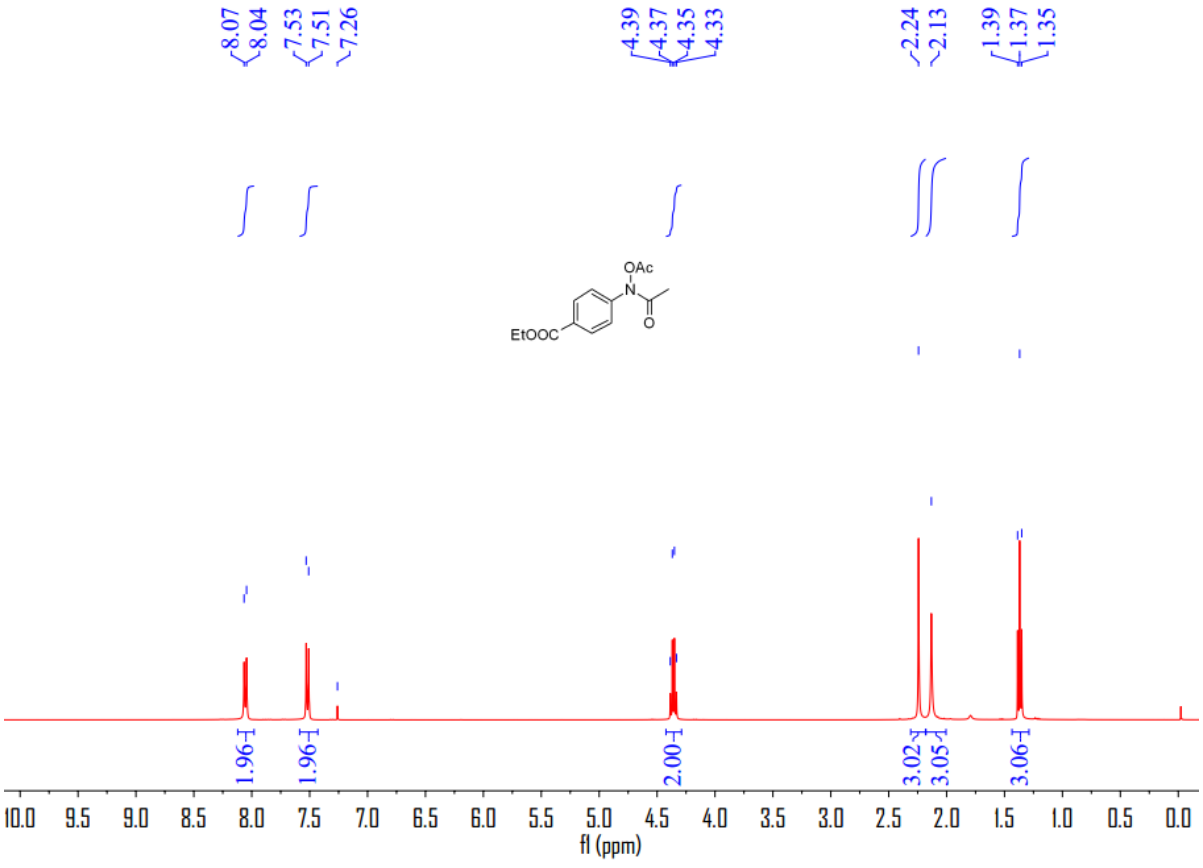
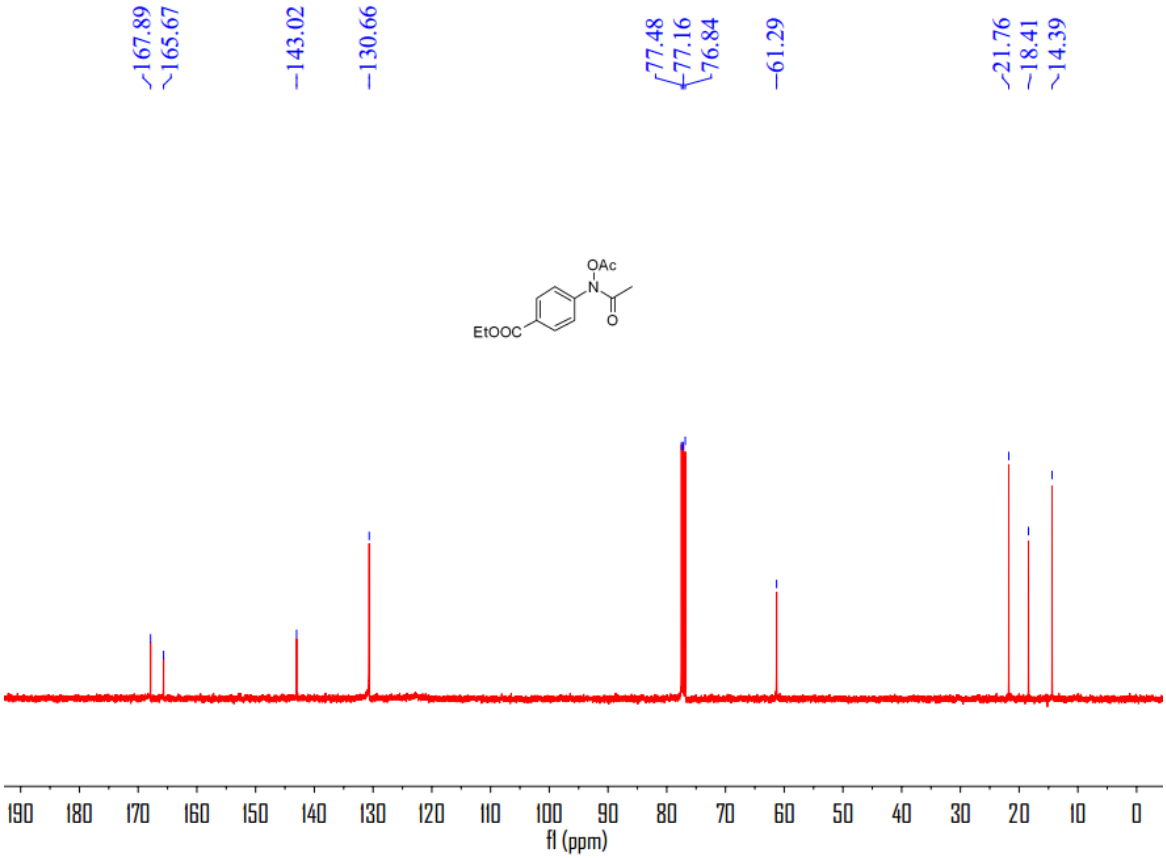
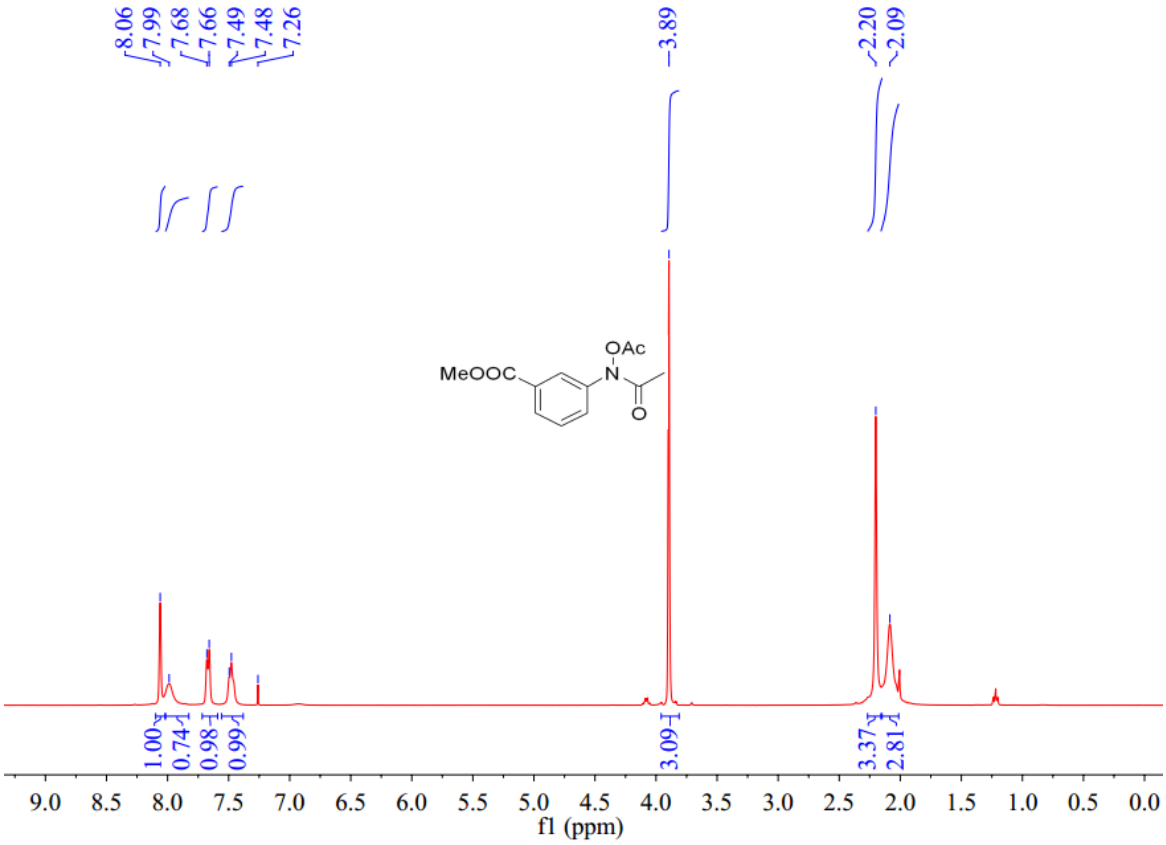


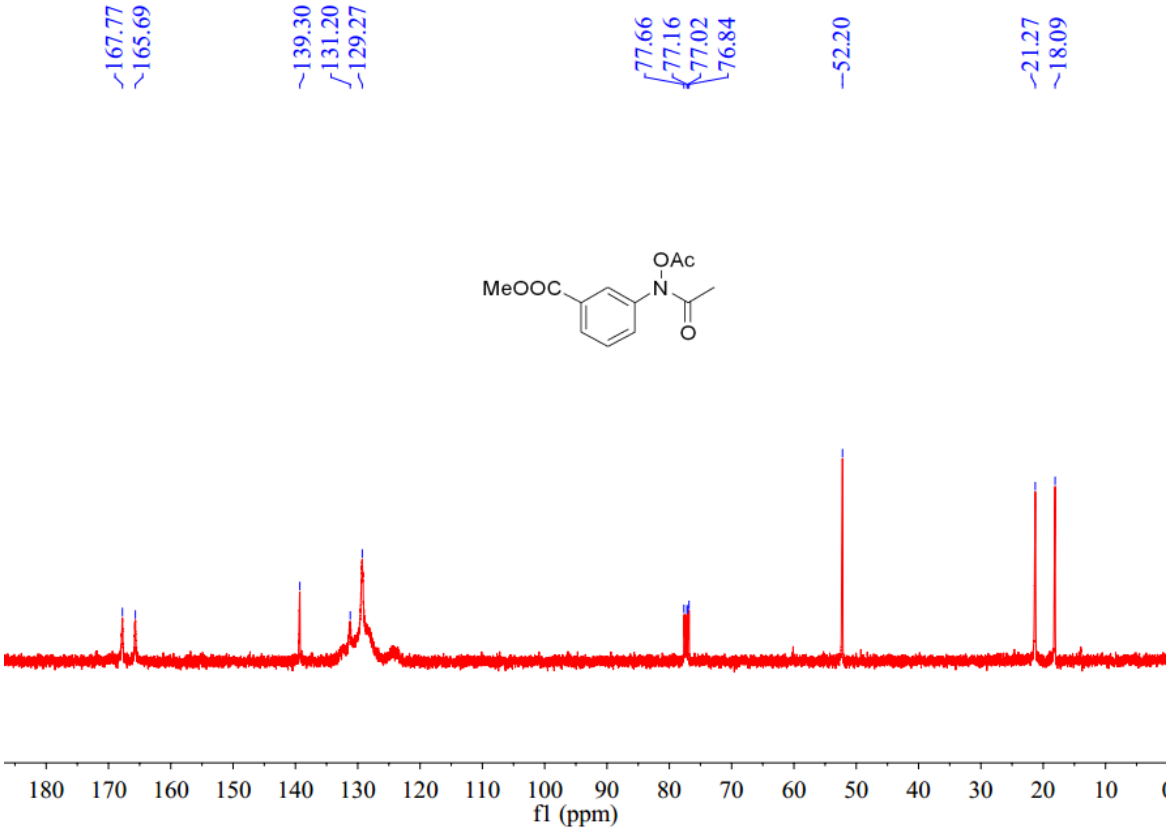
^{13}C NMR of **6p**



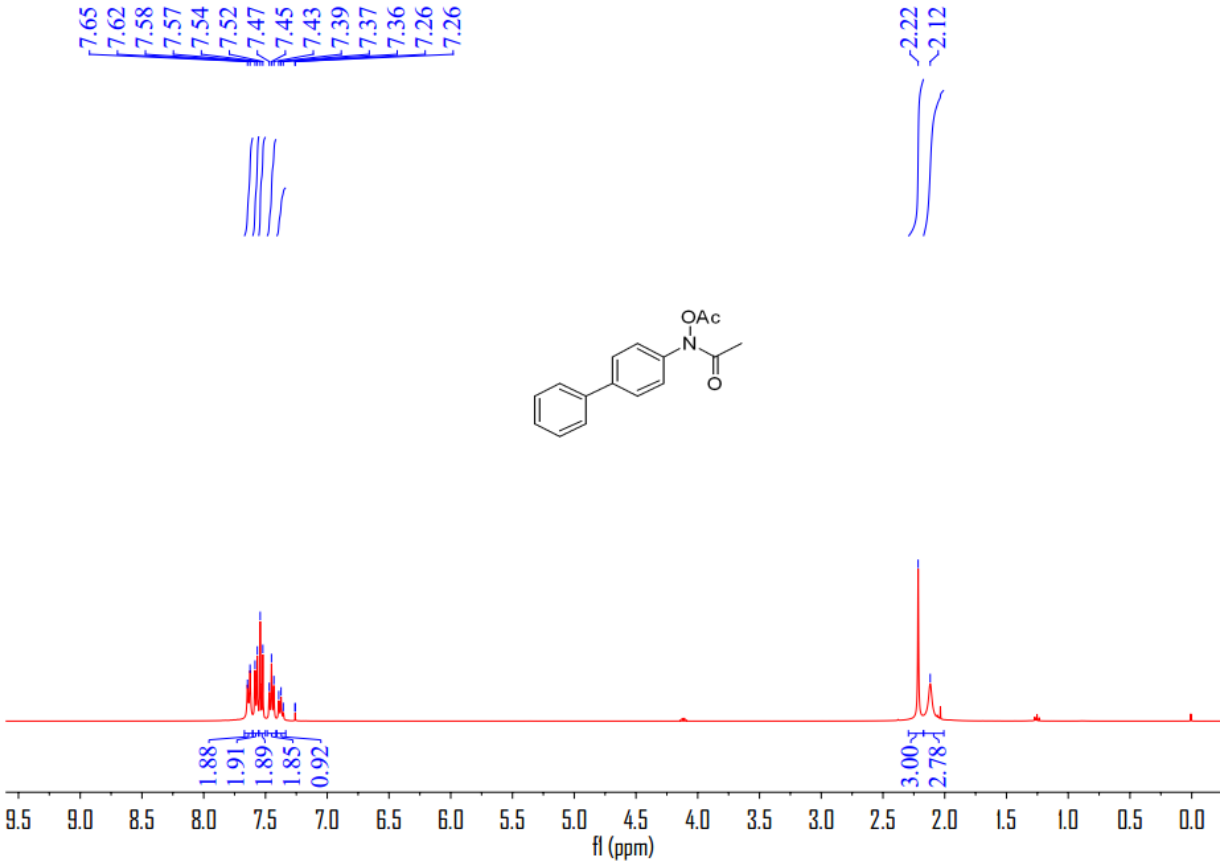
^{1}H NMR of **6q**



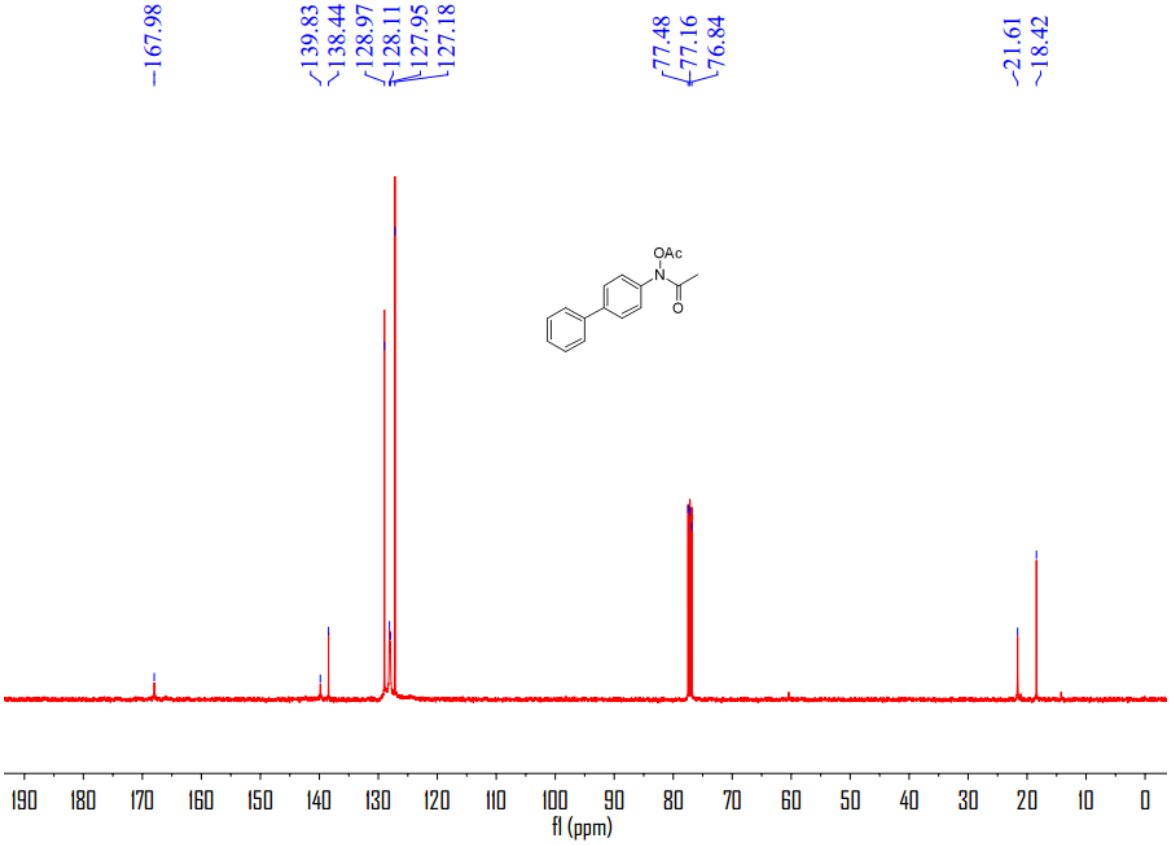
^{13}C NMR of **6q**



^{1}H NMR of **6r**



^{13}C NMR of **6r**



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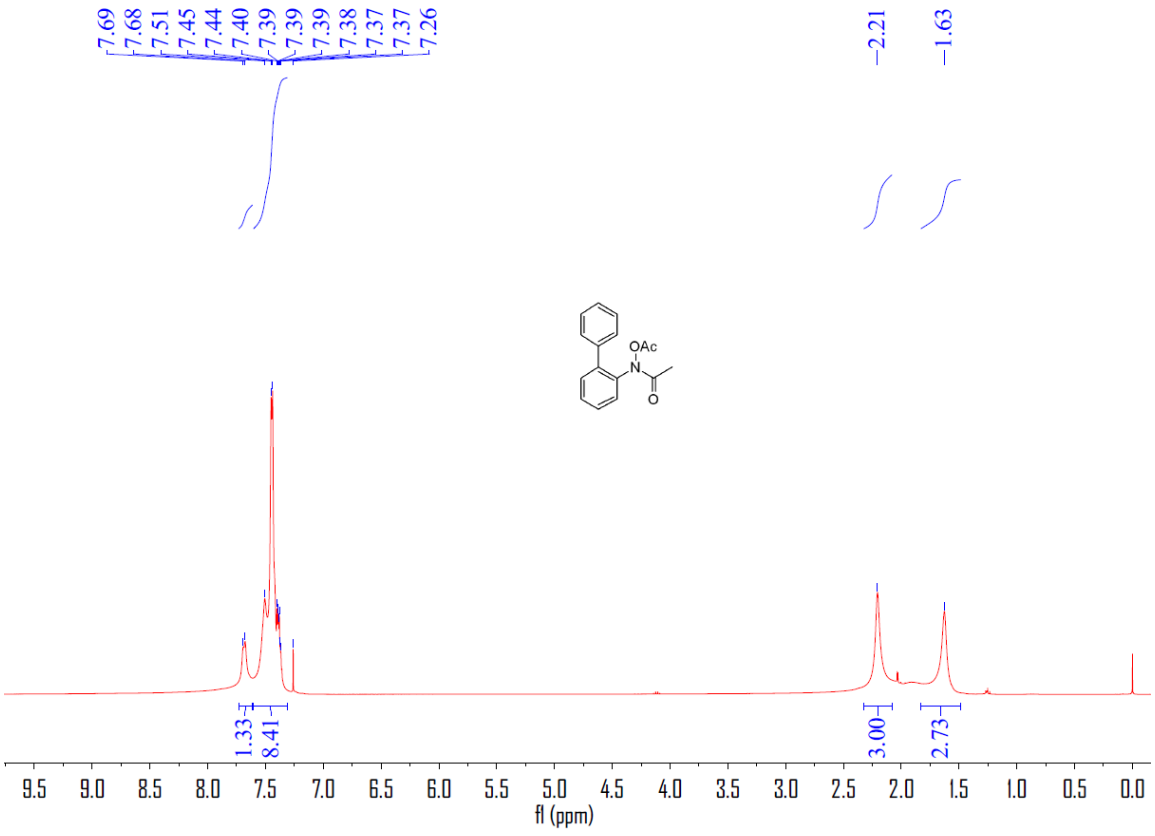

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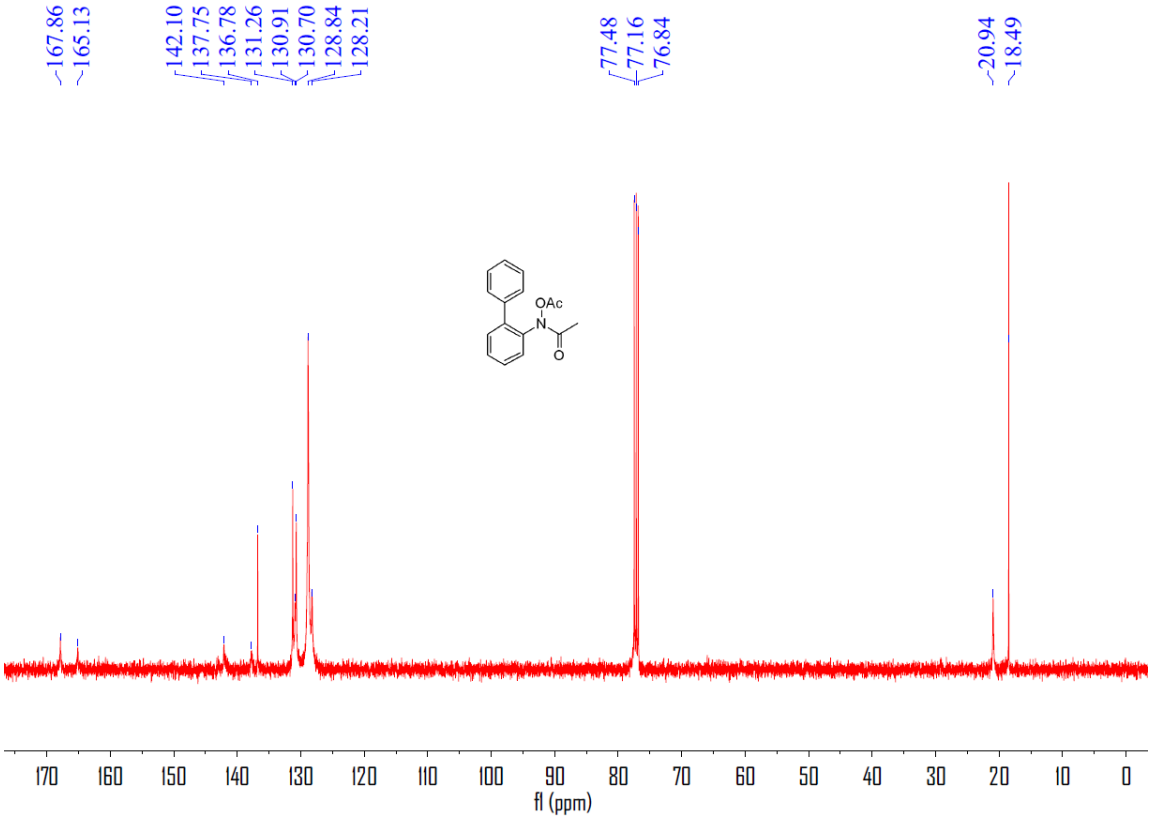

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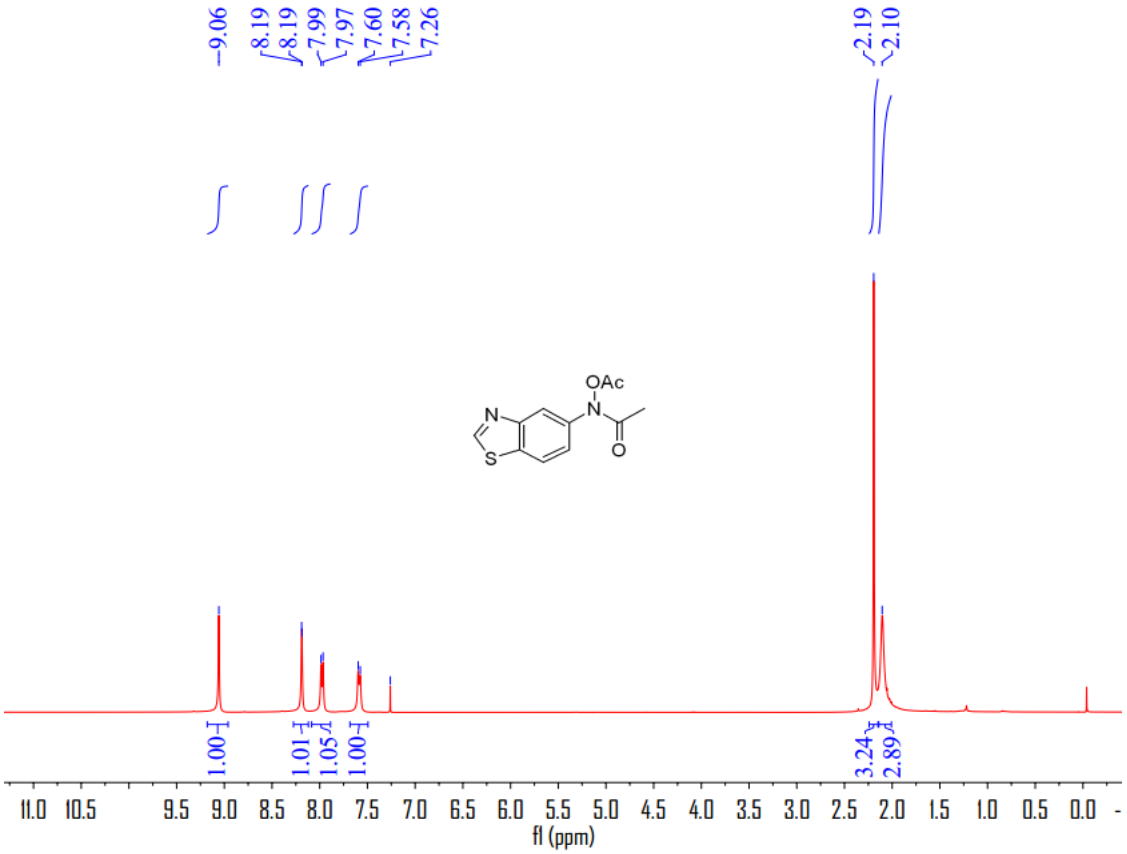

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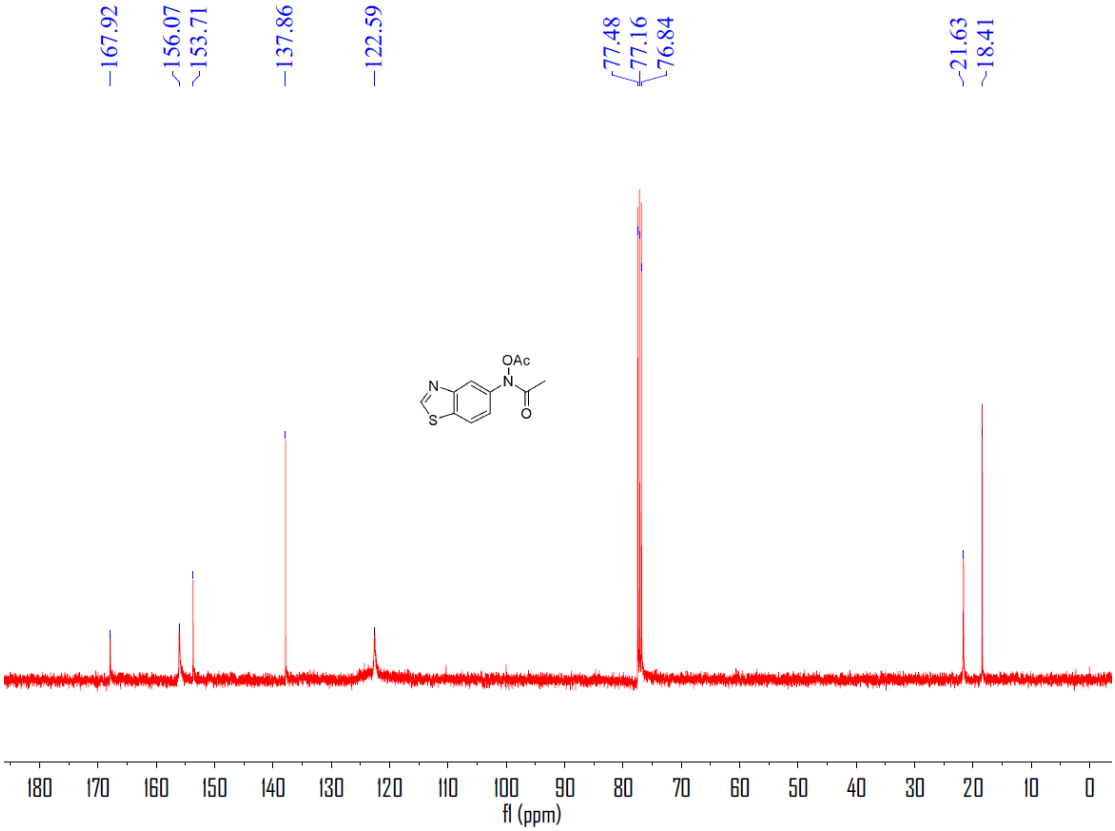
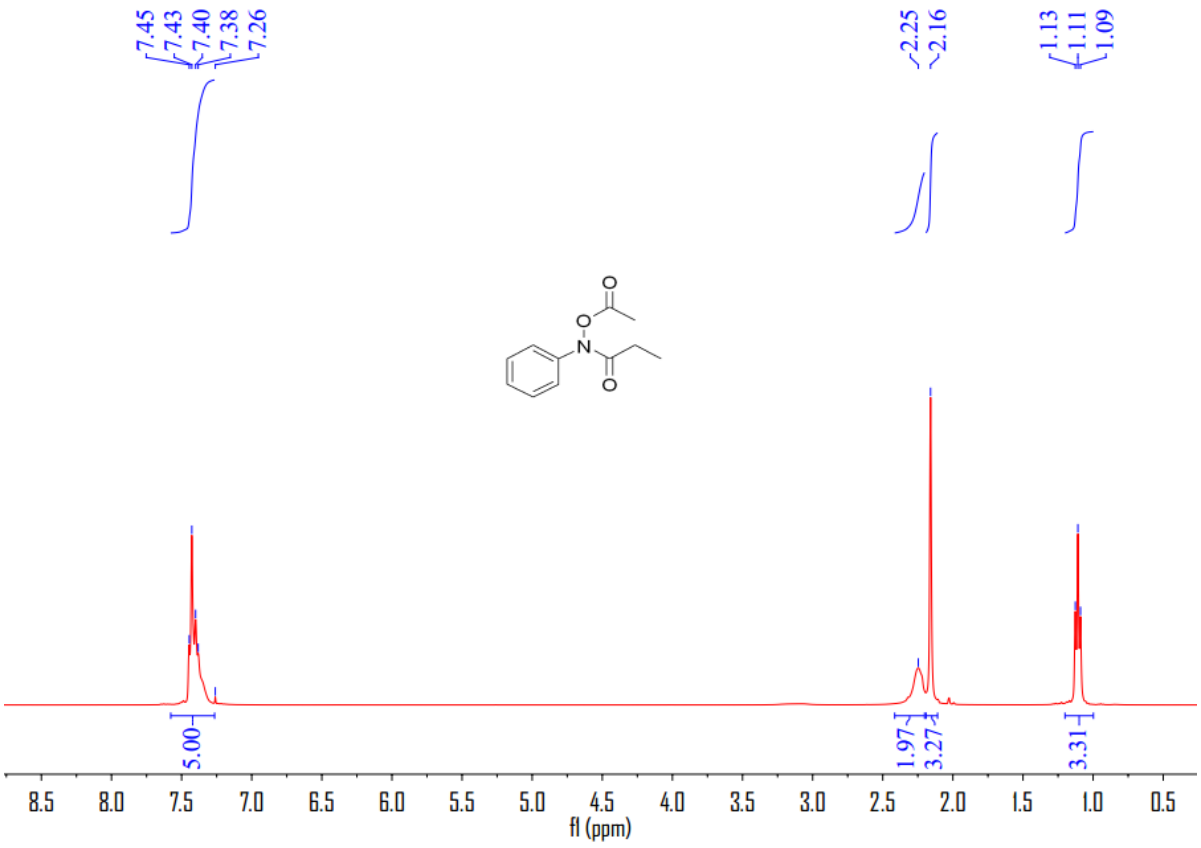


^{1}H NMR of **6u**



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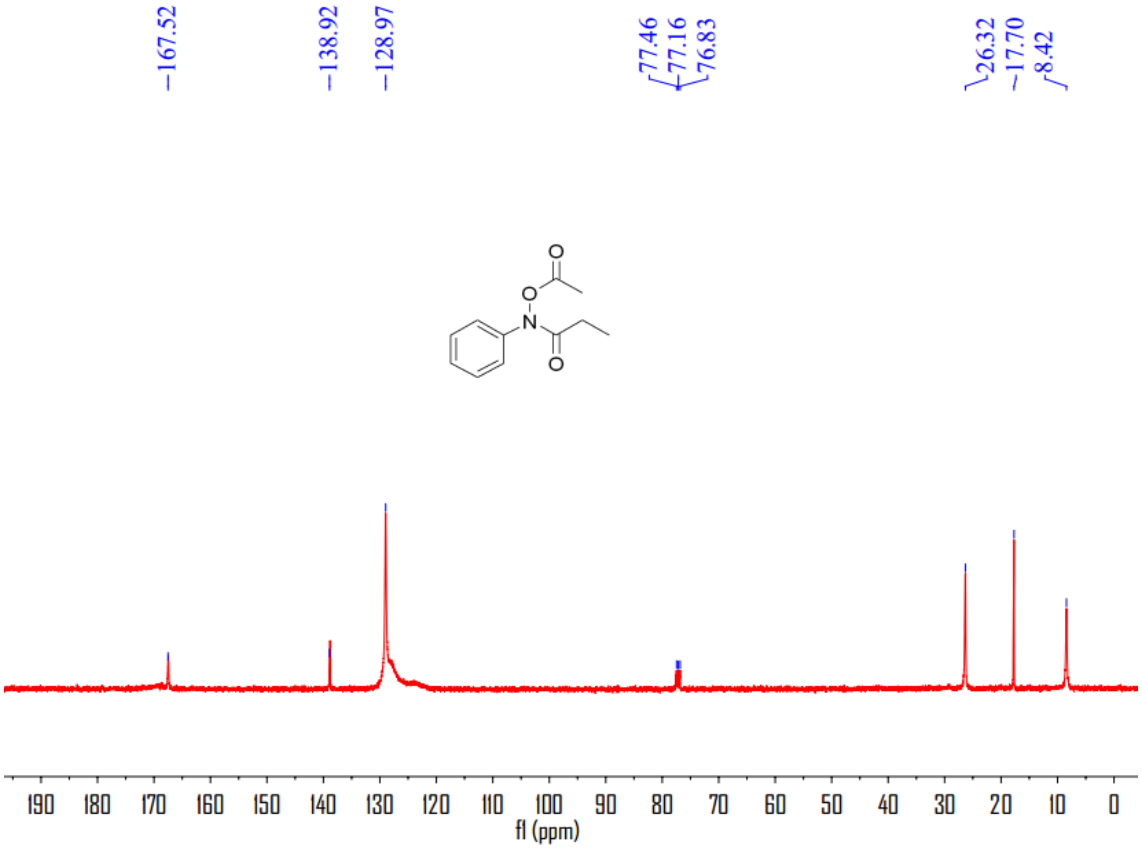
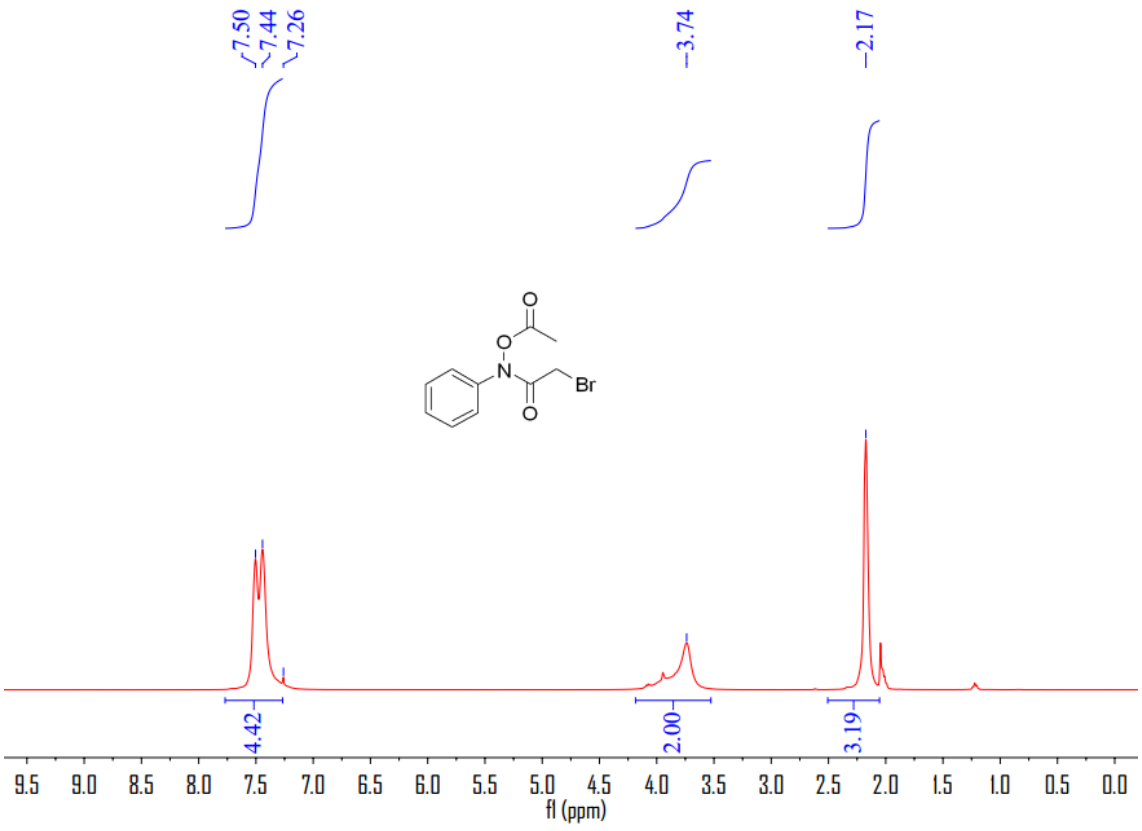


^{1}H NMR of **6v**



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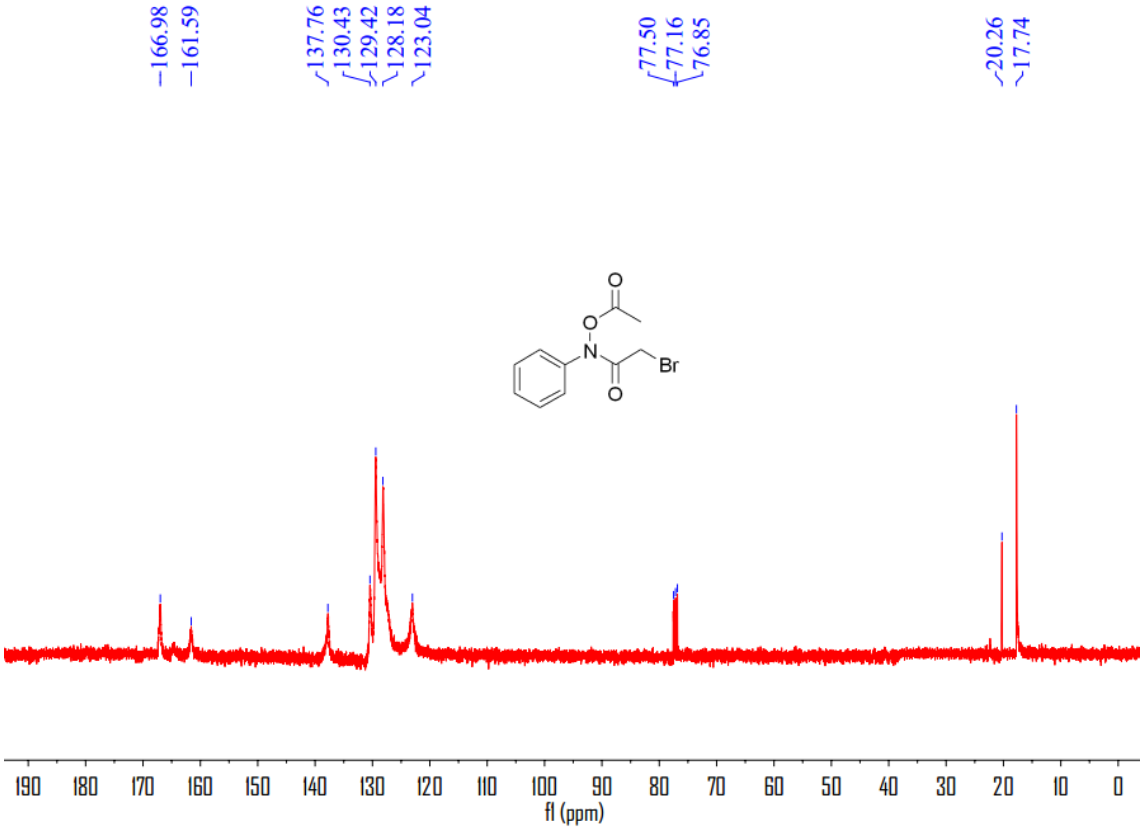
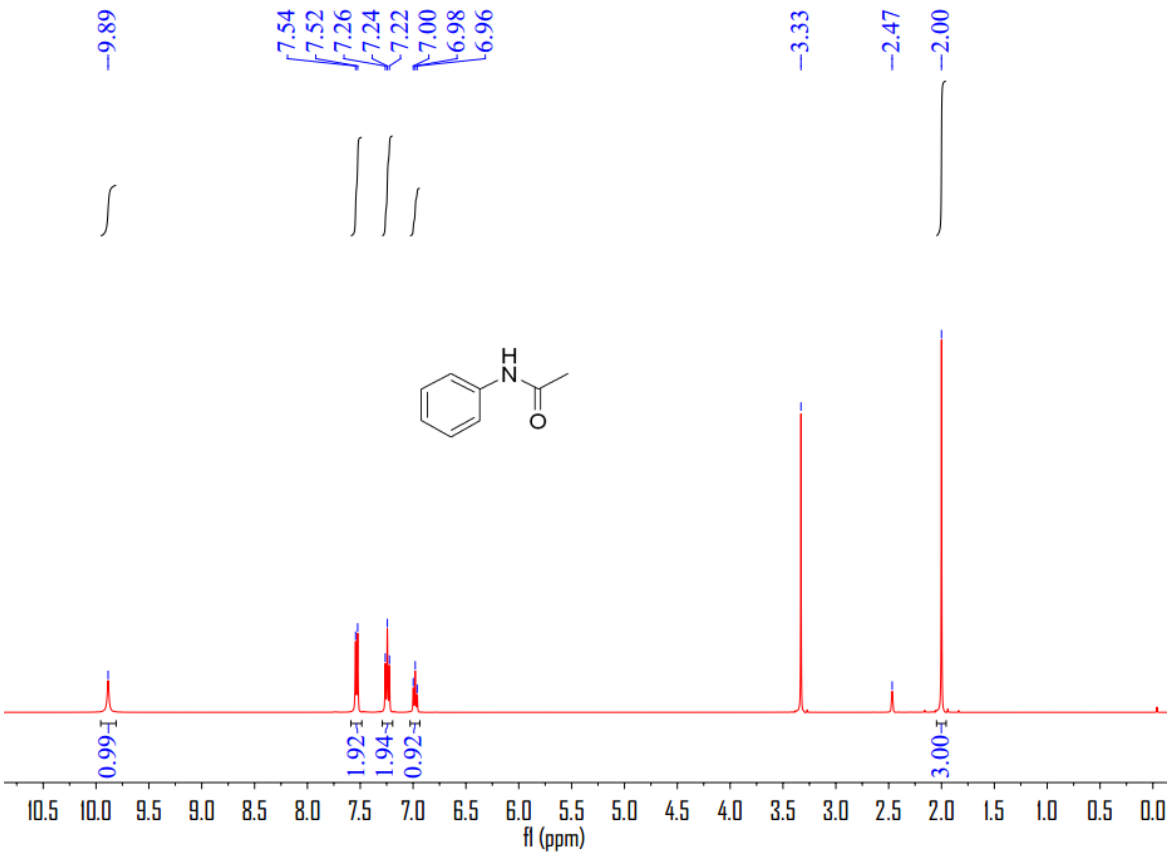


^{1}H NMR of **4a**



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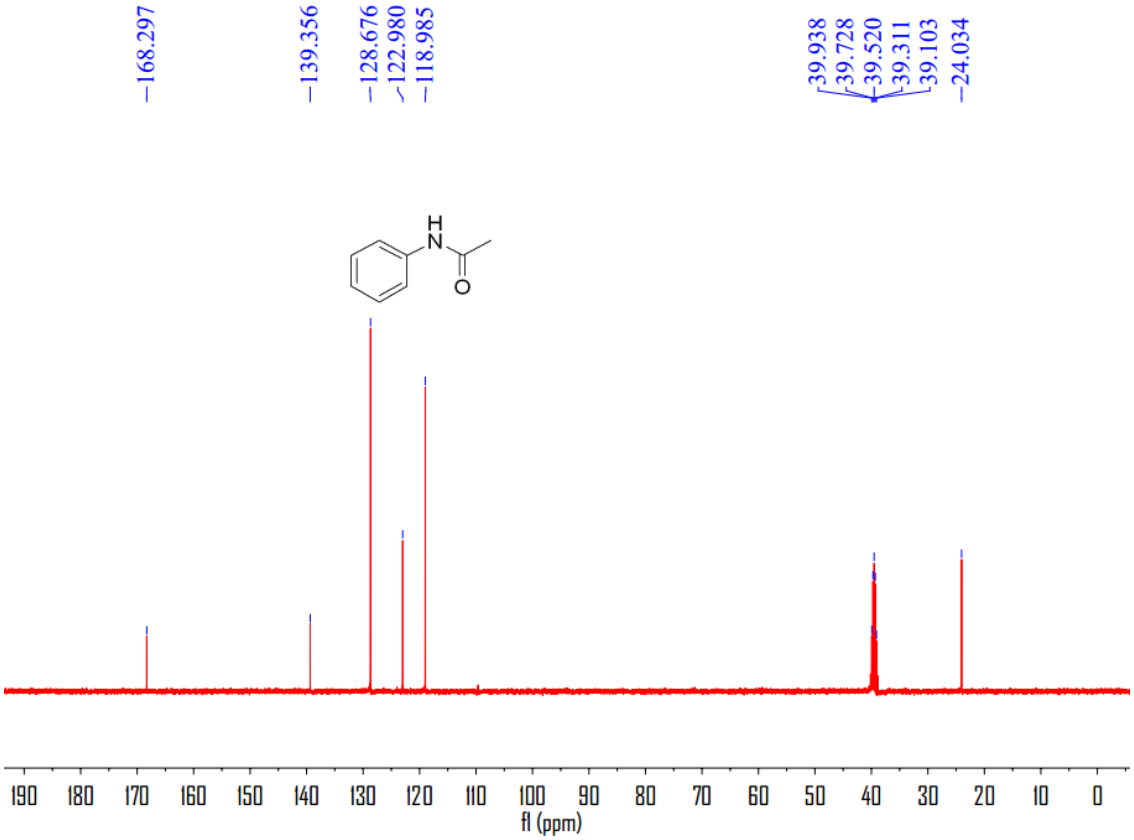
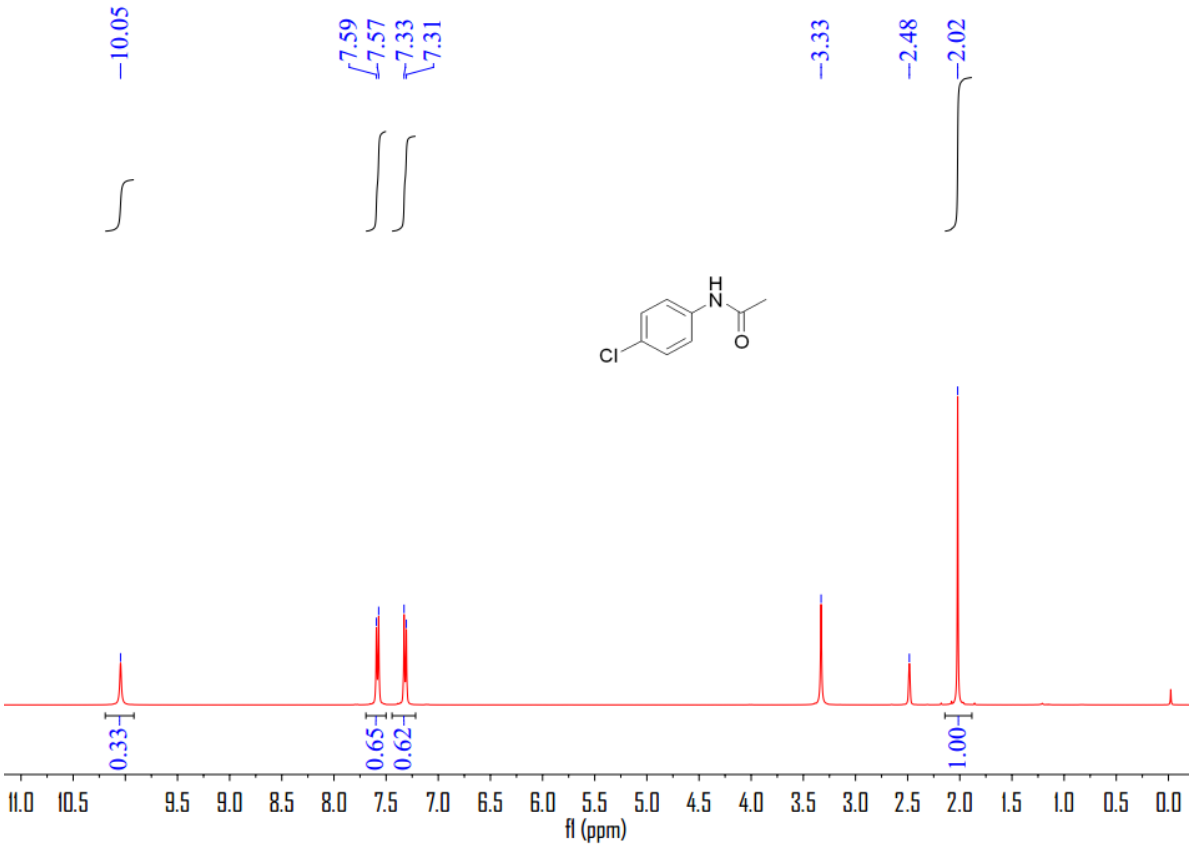


^{1}H NMR of **4b**



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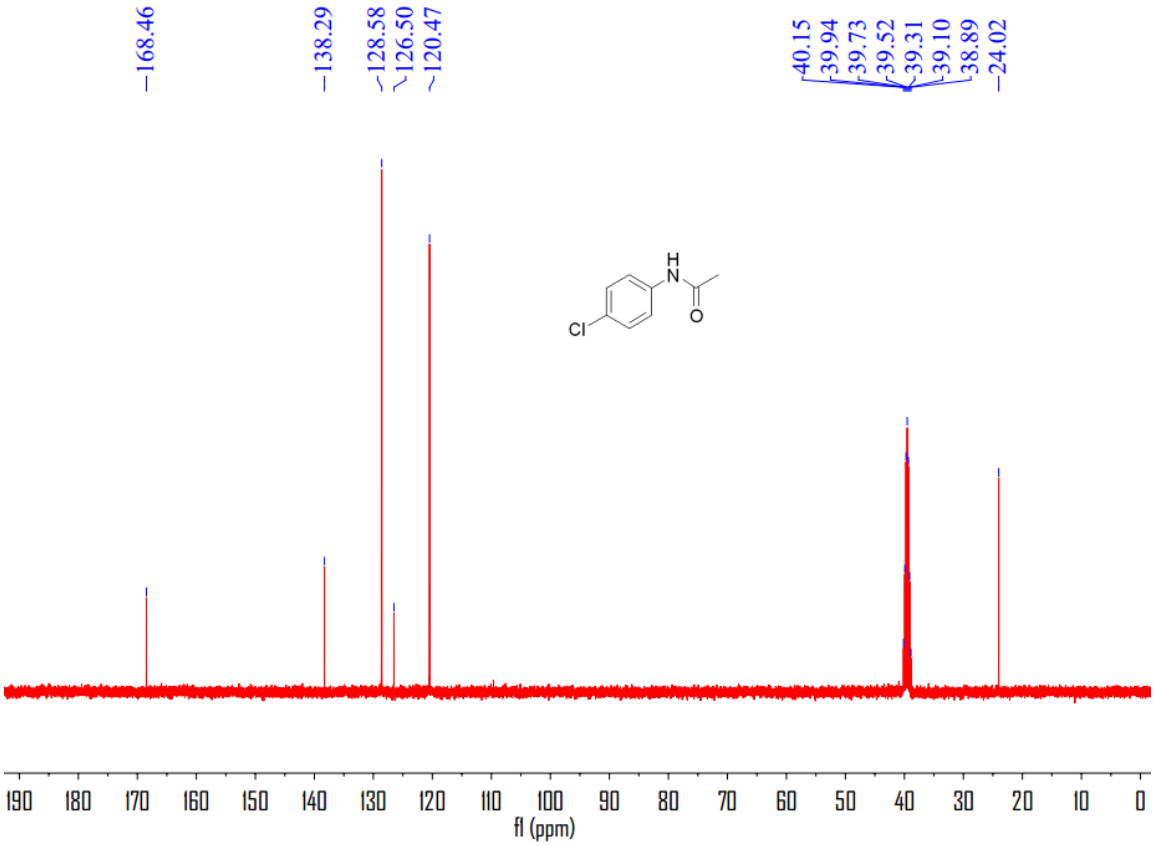

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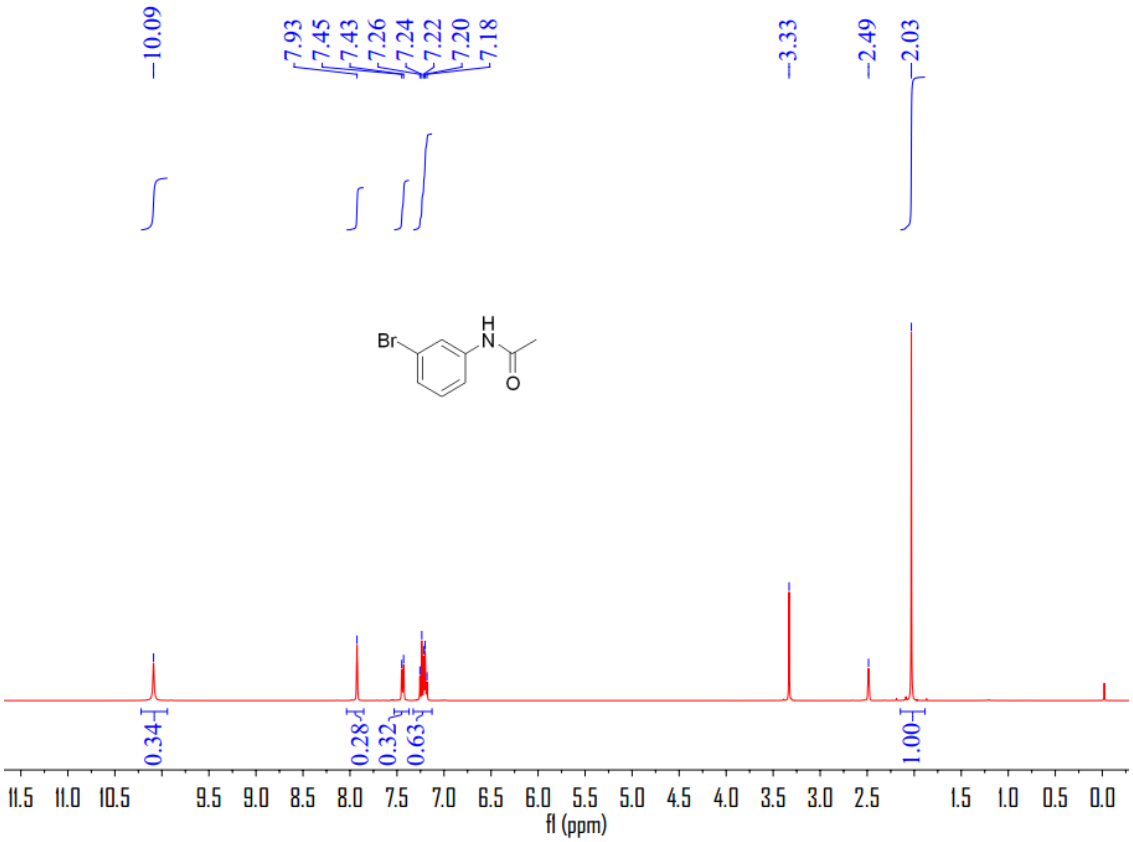

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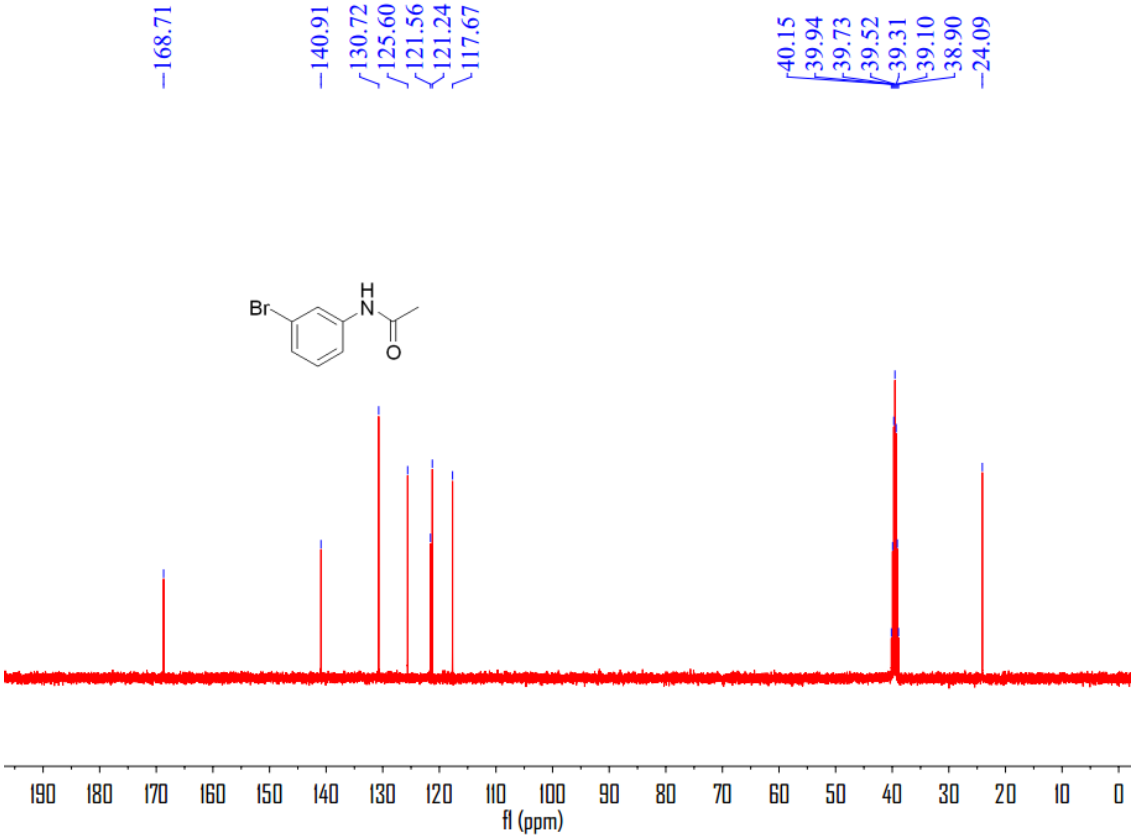

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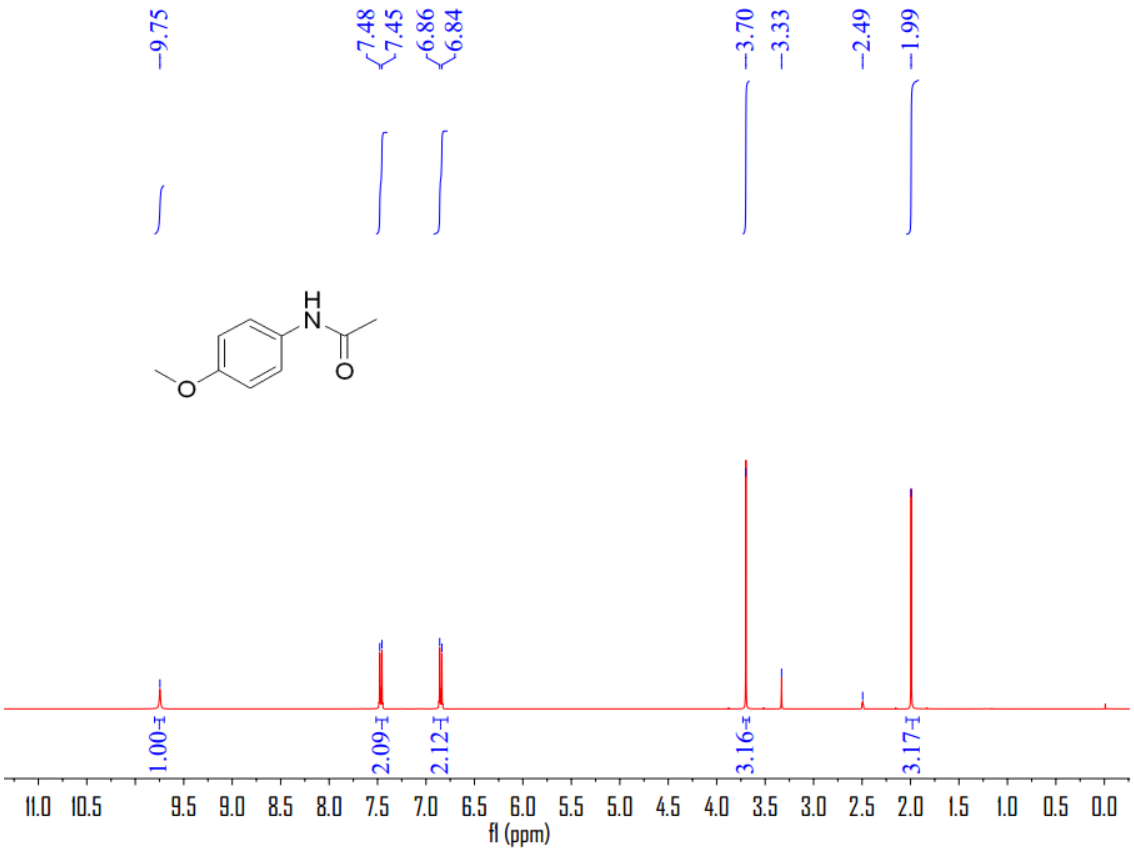

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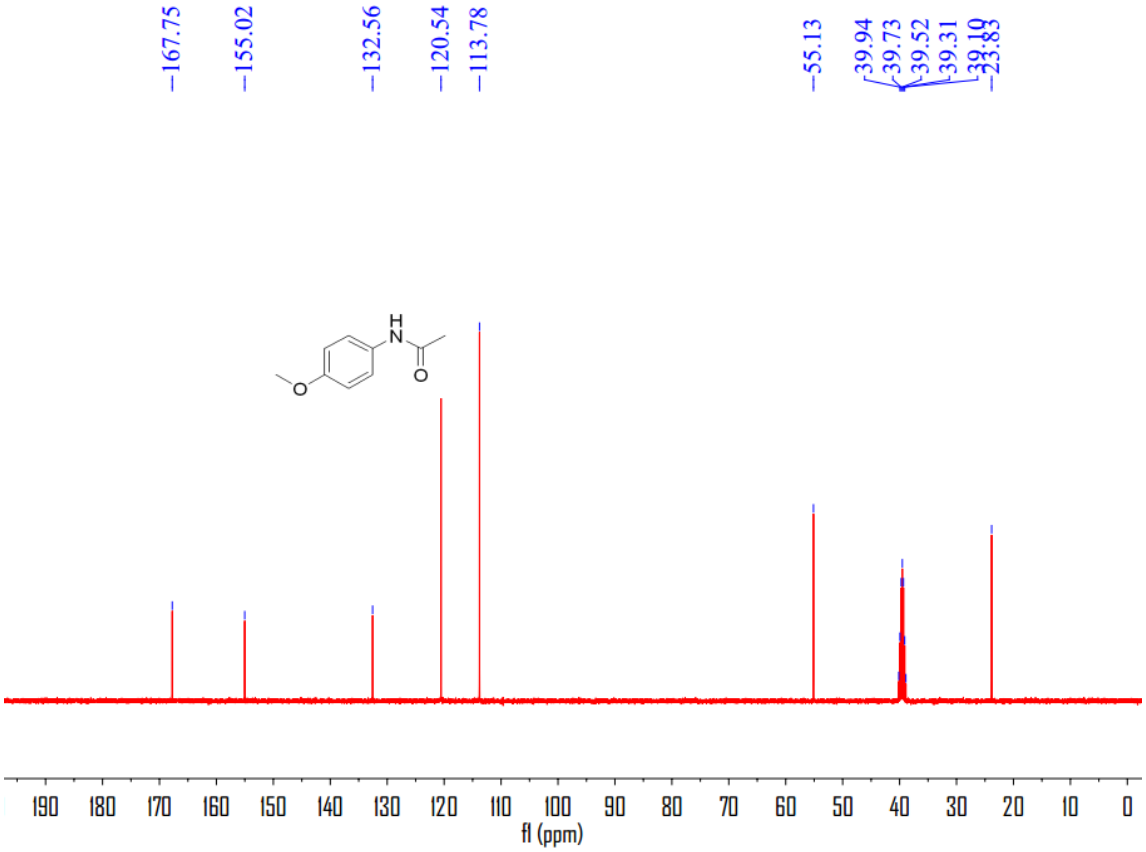

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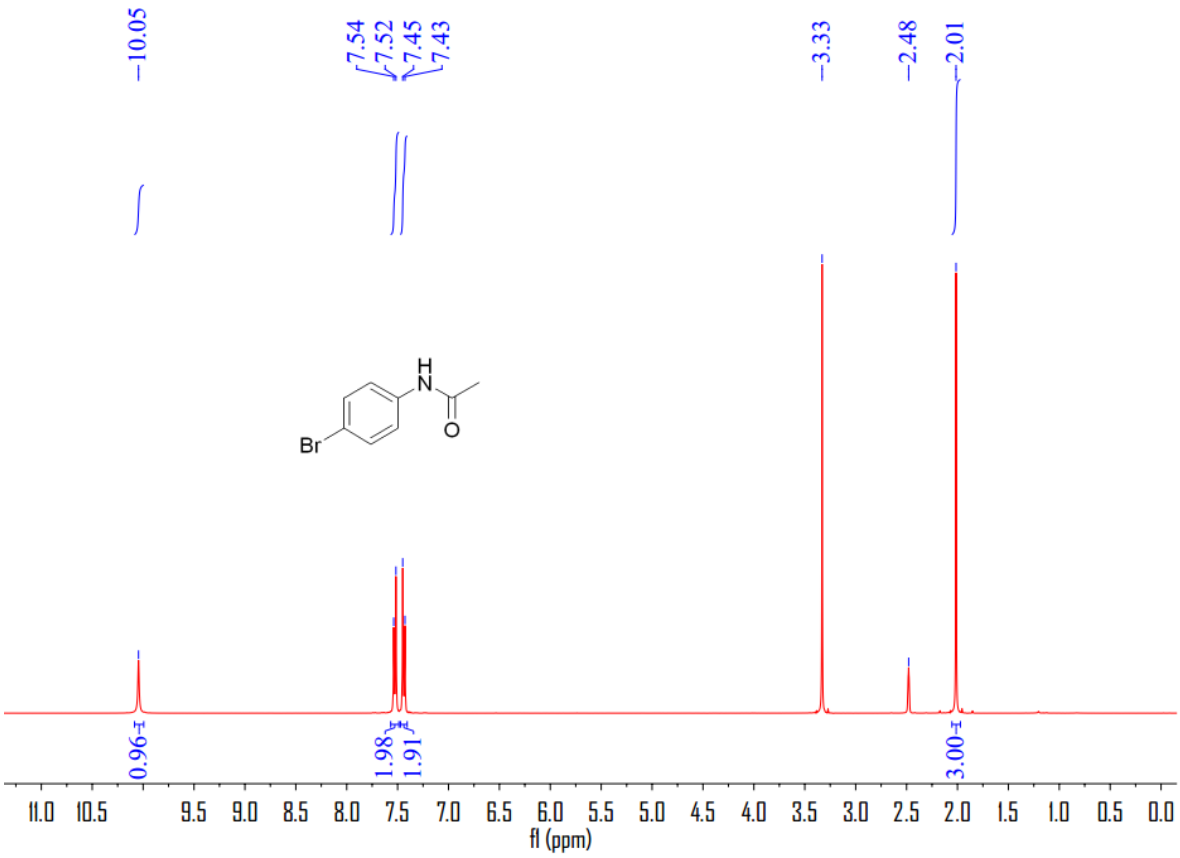
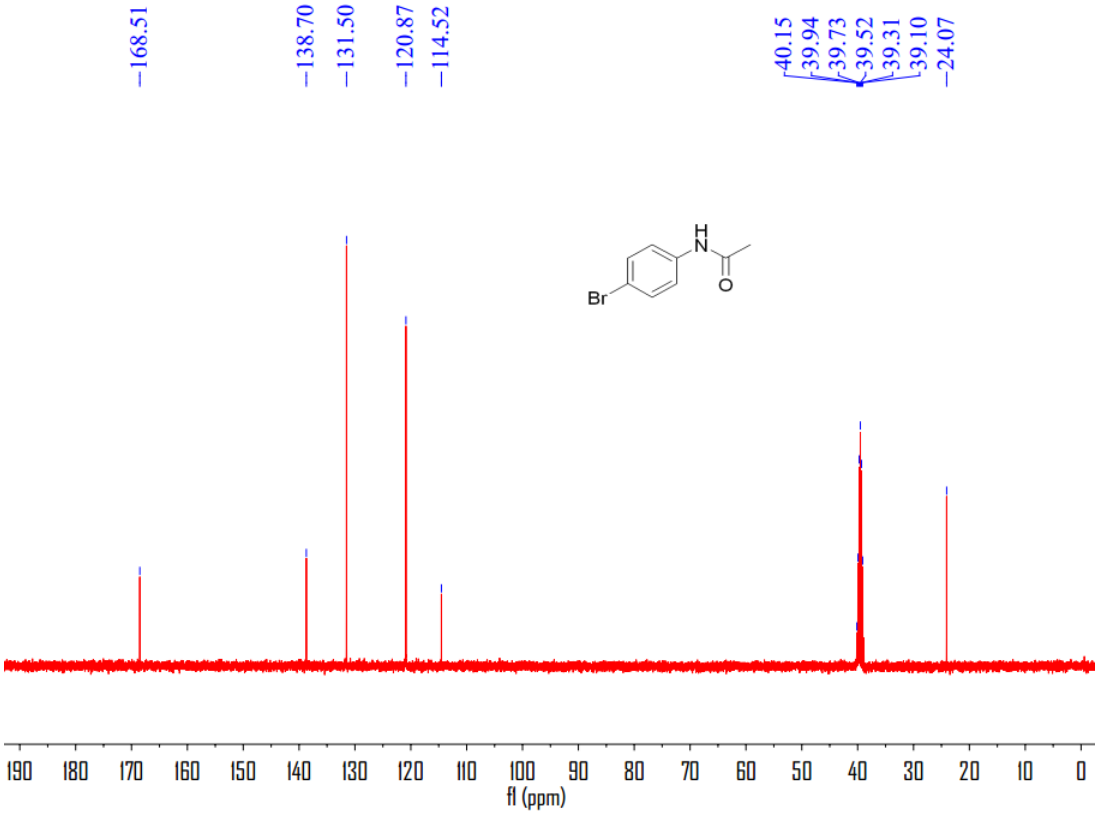
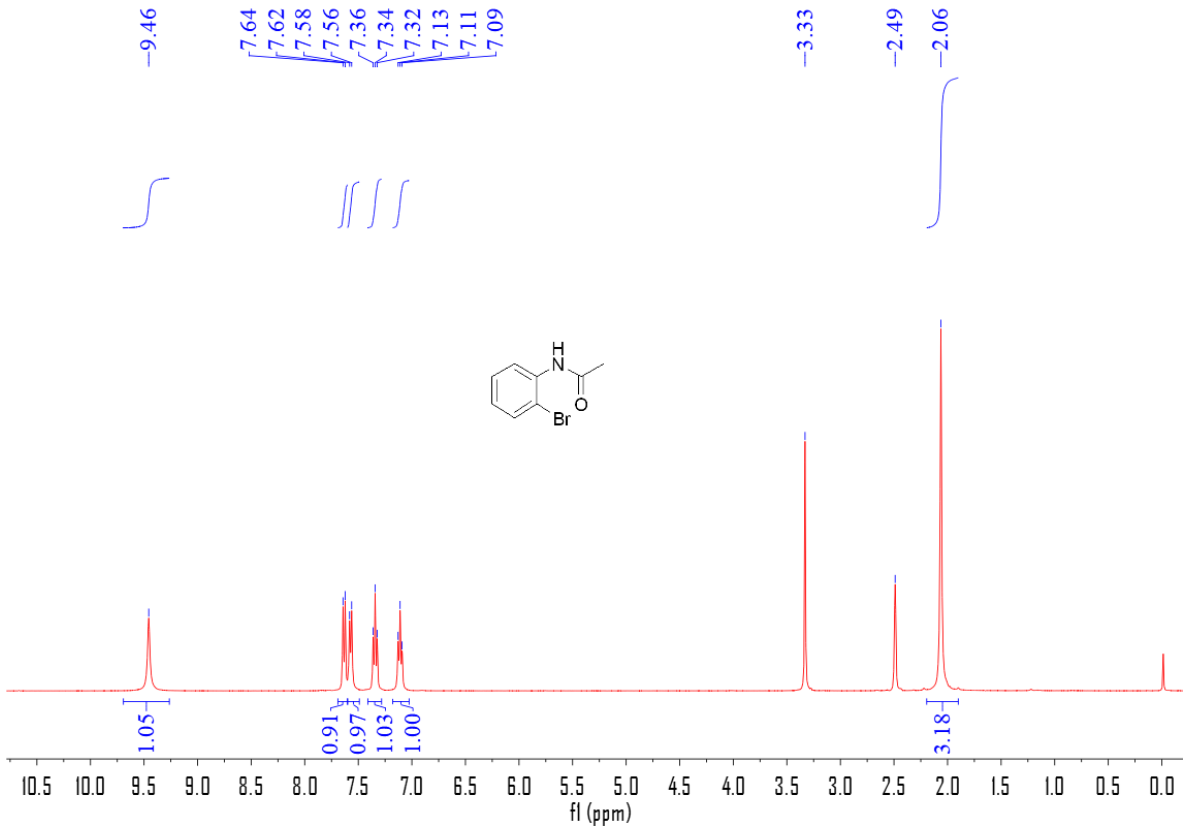


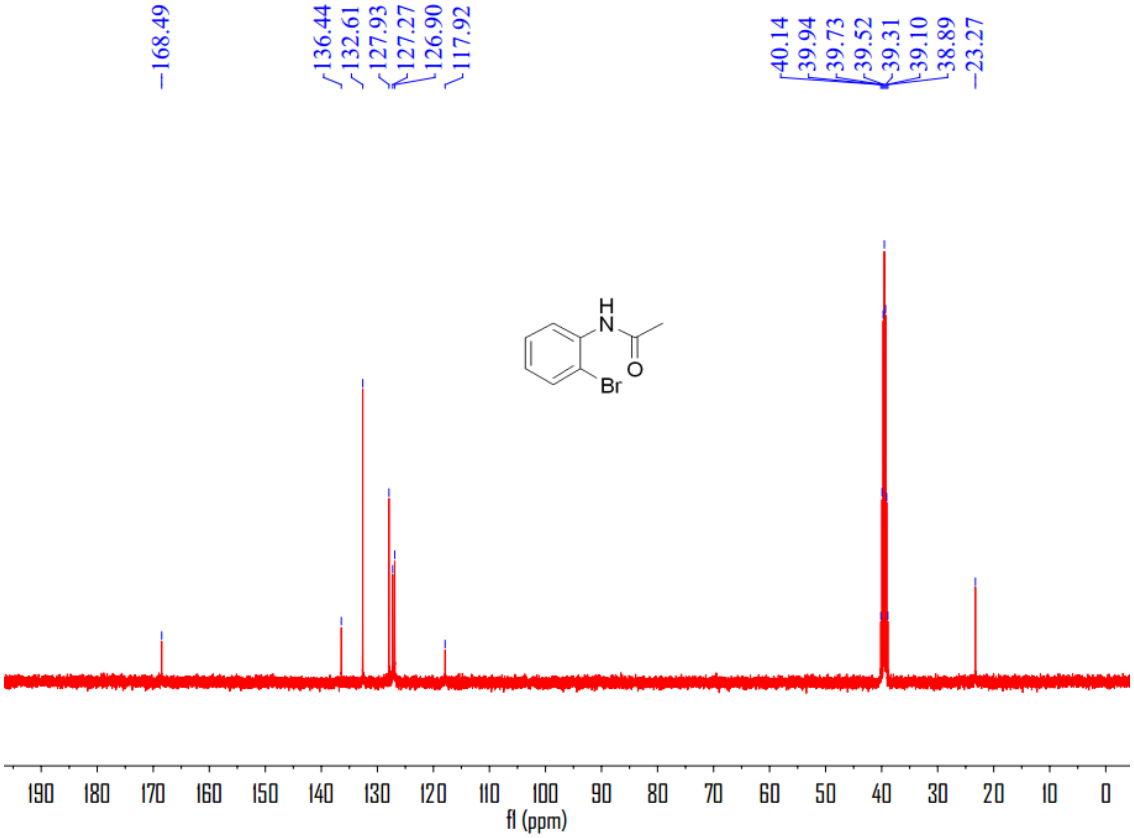
^{13}C NMR of **4e**



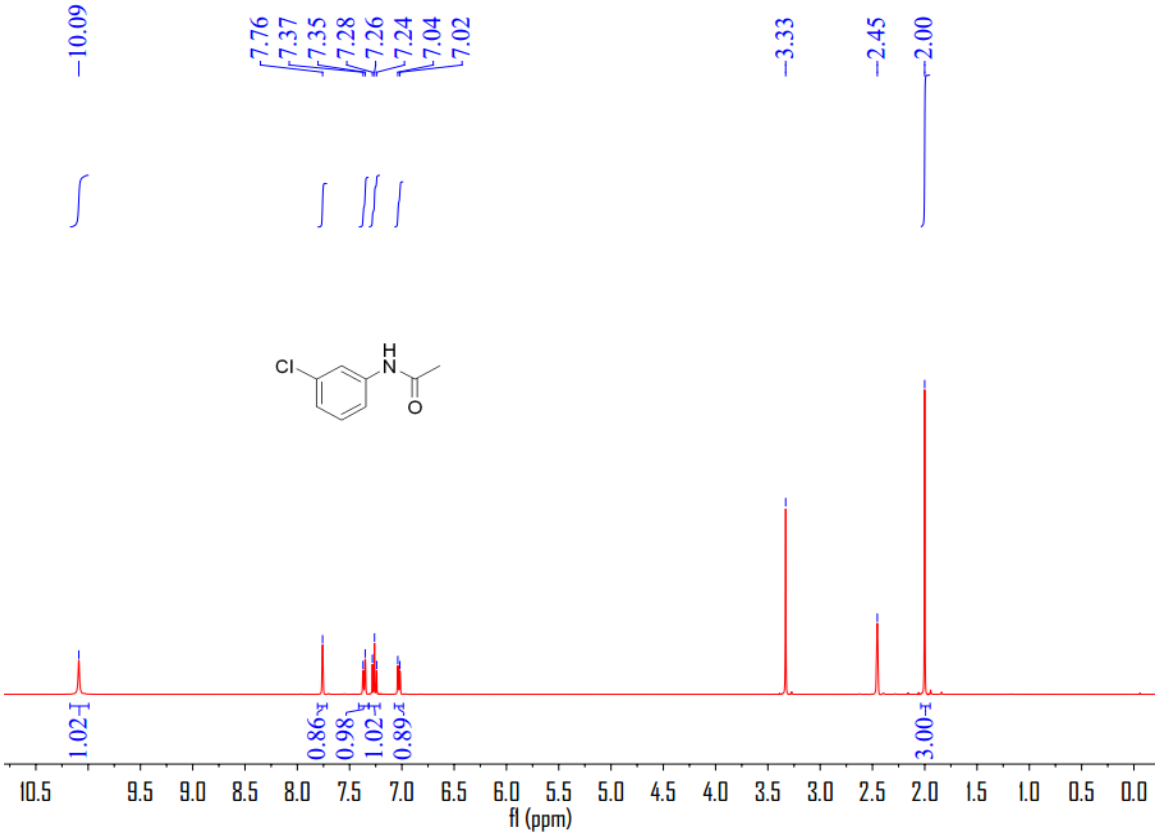
^{1}H NMR of **4f**



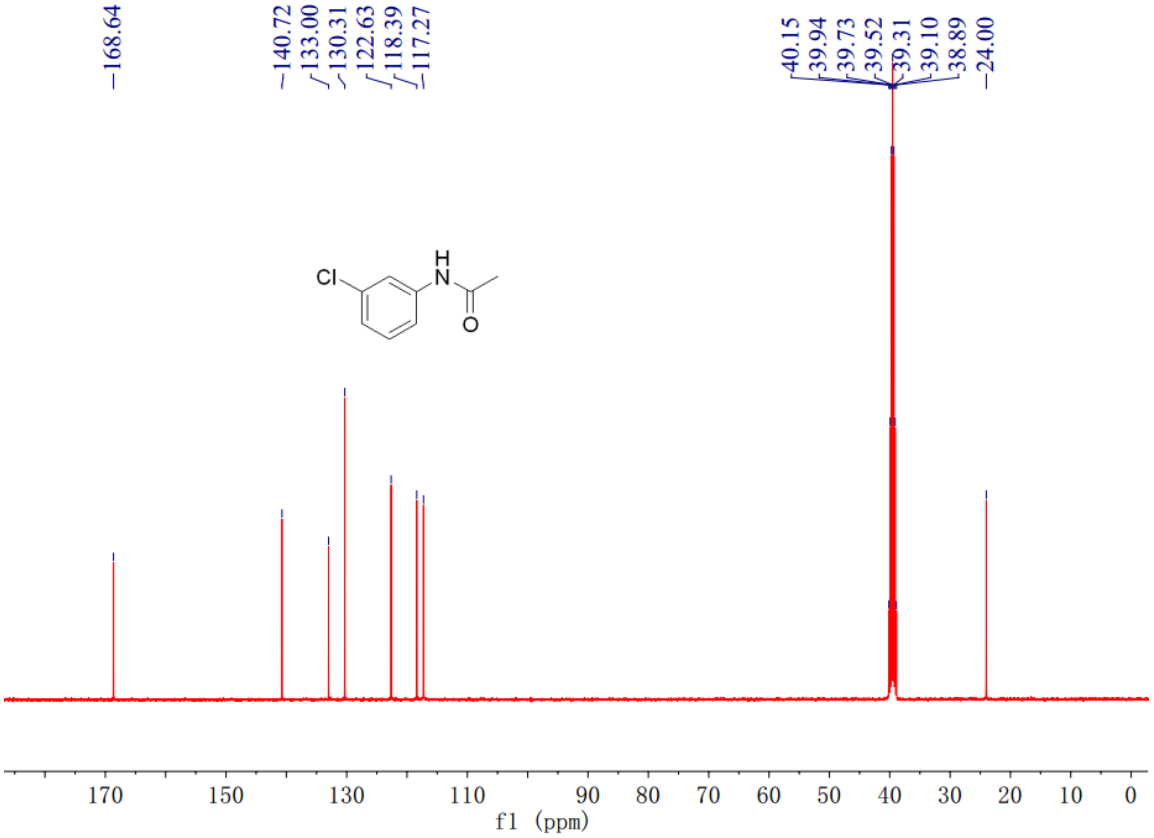
^{13}C NMR of **4f**



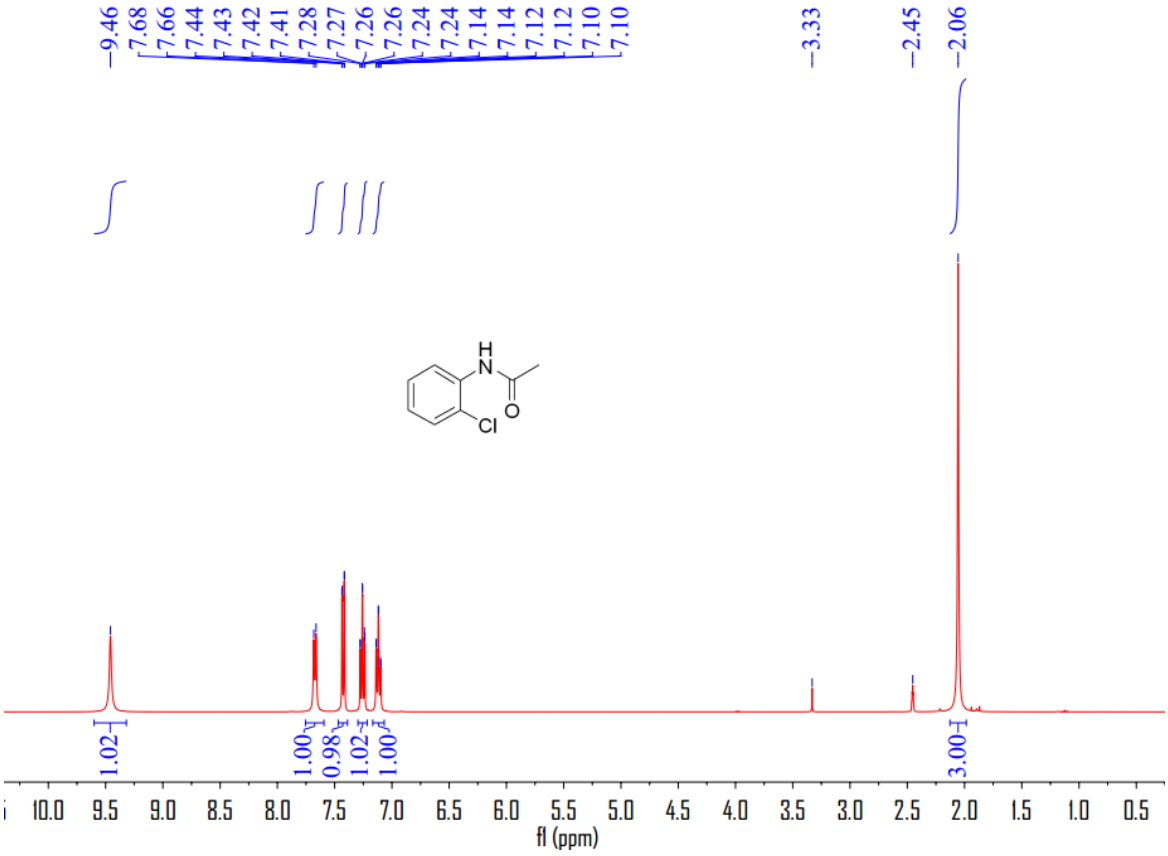
^{1}H NMR of **4g**



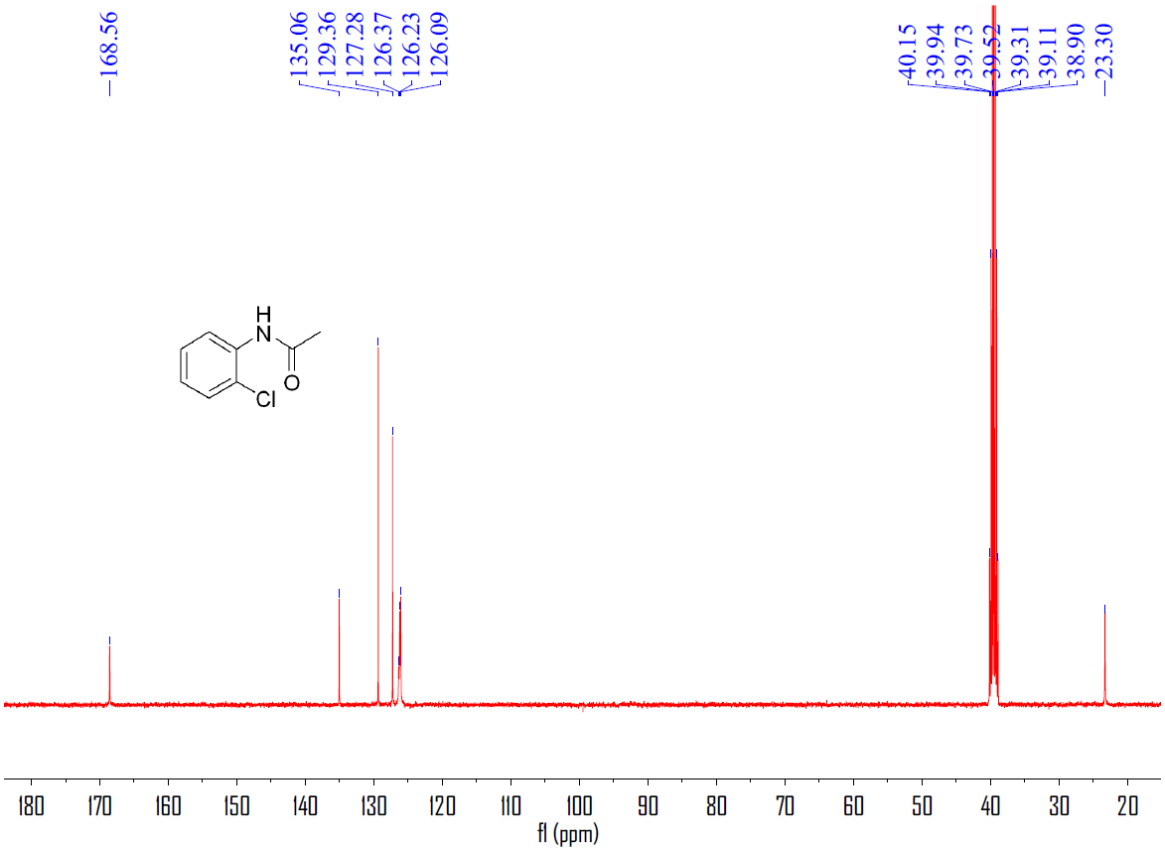
^{13}C NMR of **4g**



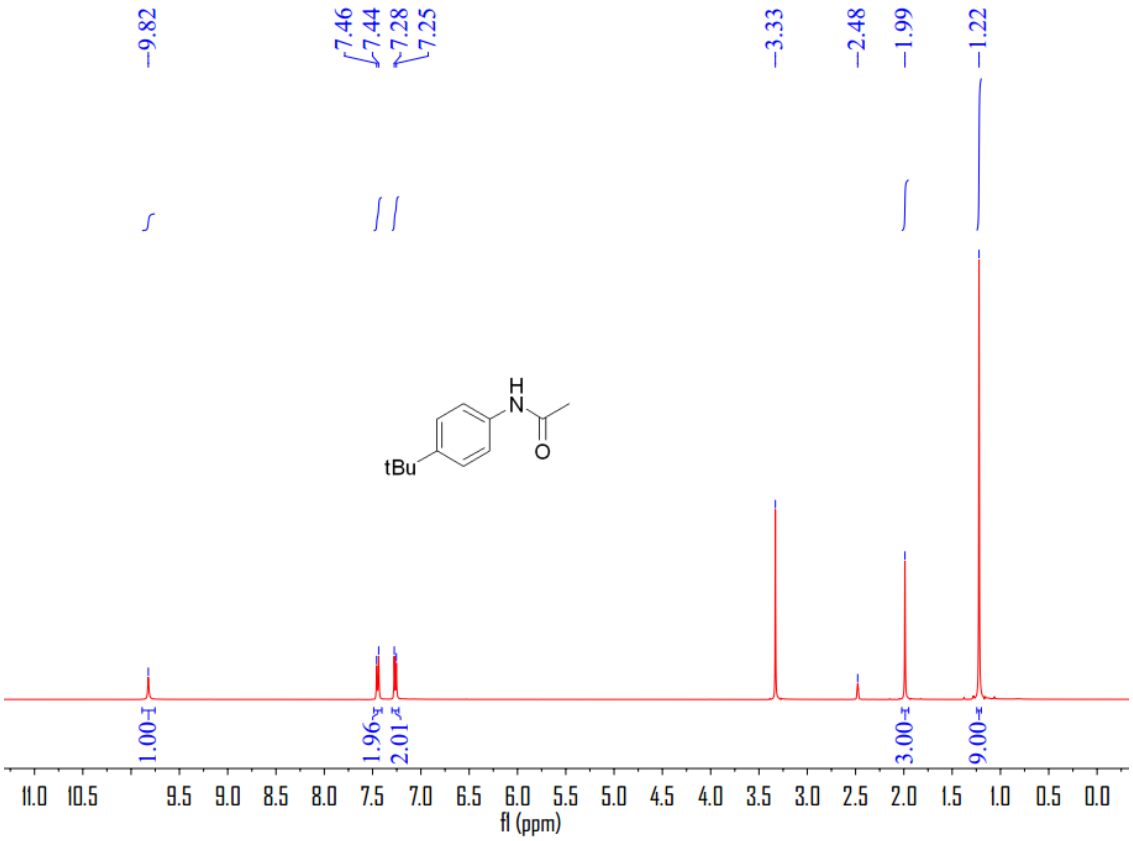
^{1}H NMR of **4h**



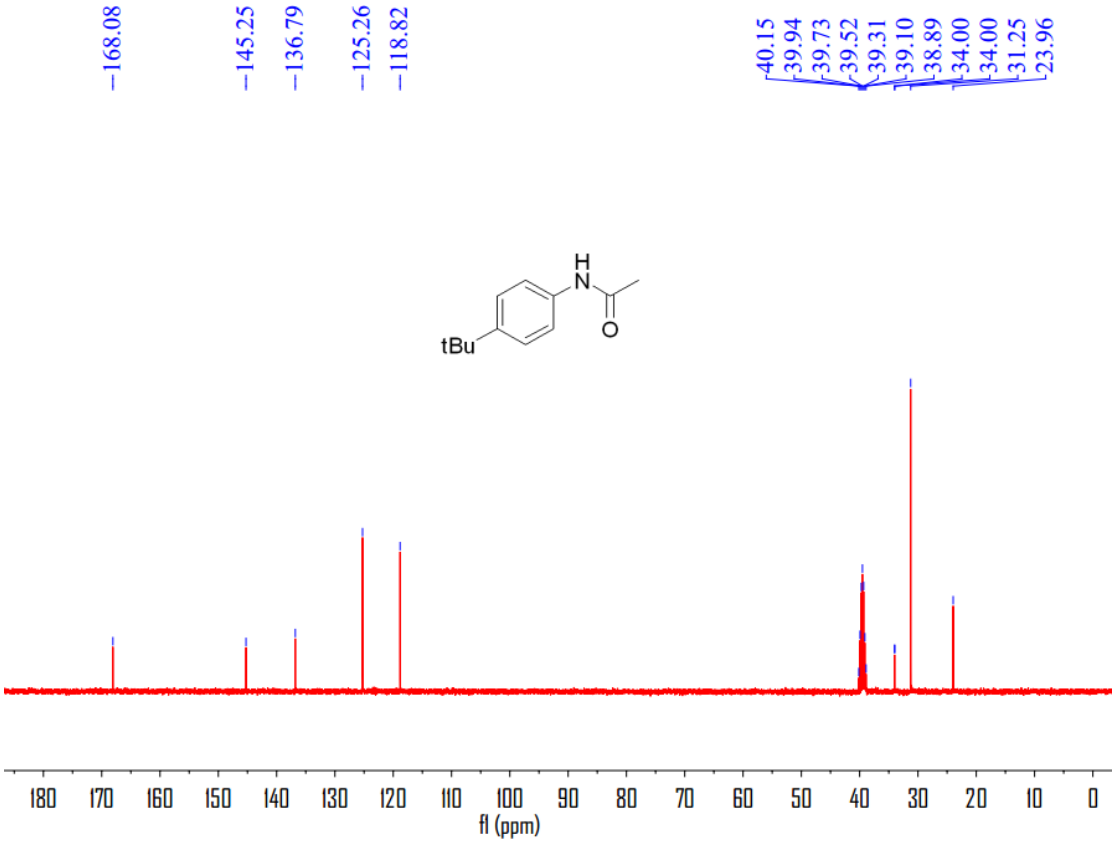
^{13}C NMR of **4h**



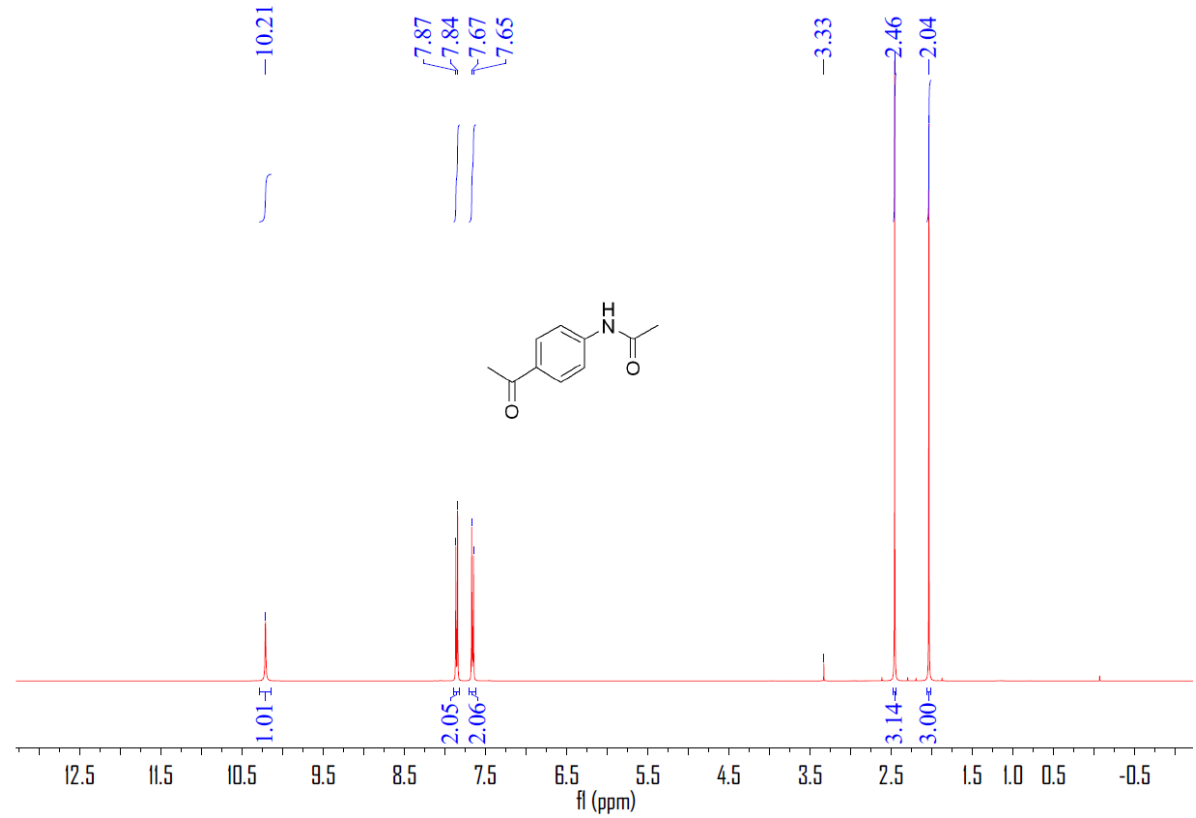
^{1}H NMR of **4i**



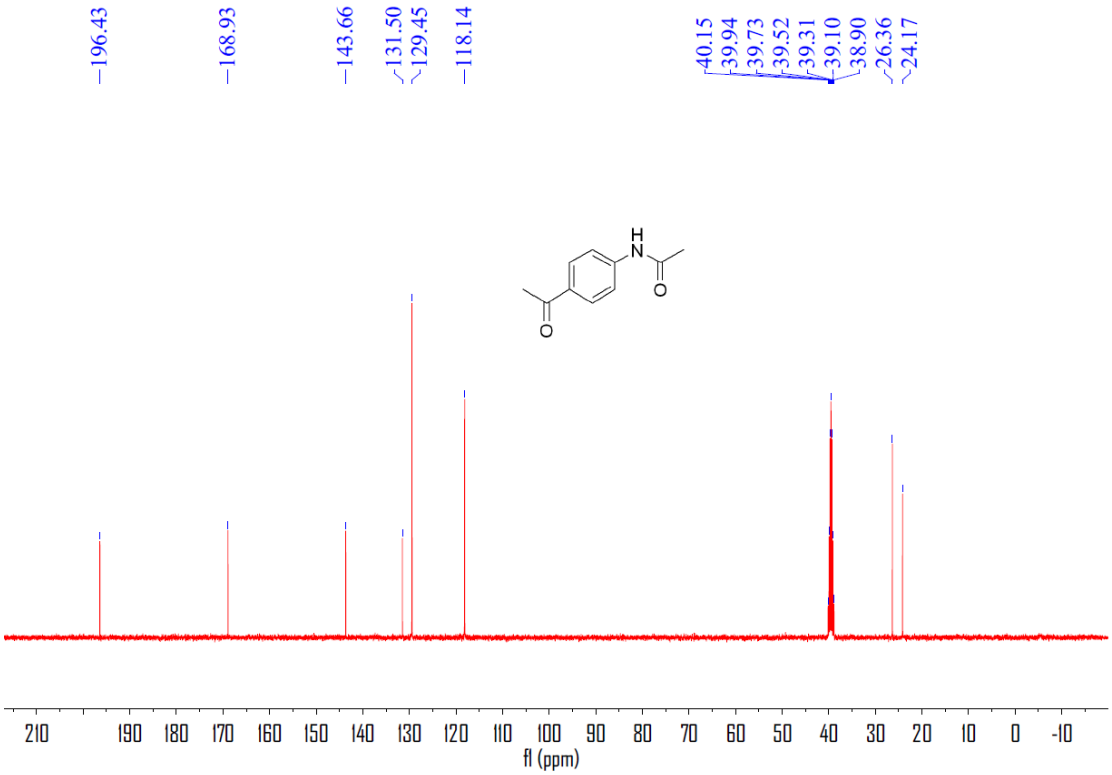
^{13}C NMR of **4i**



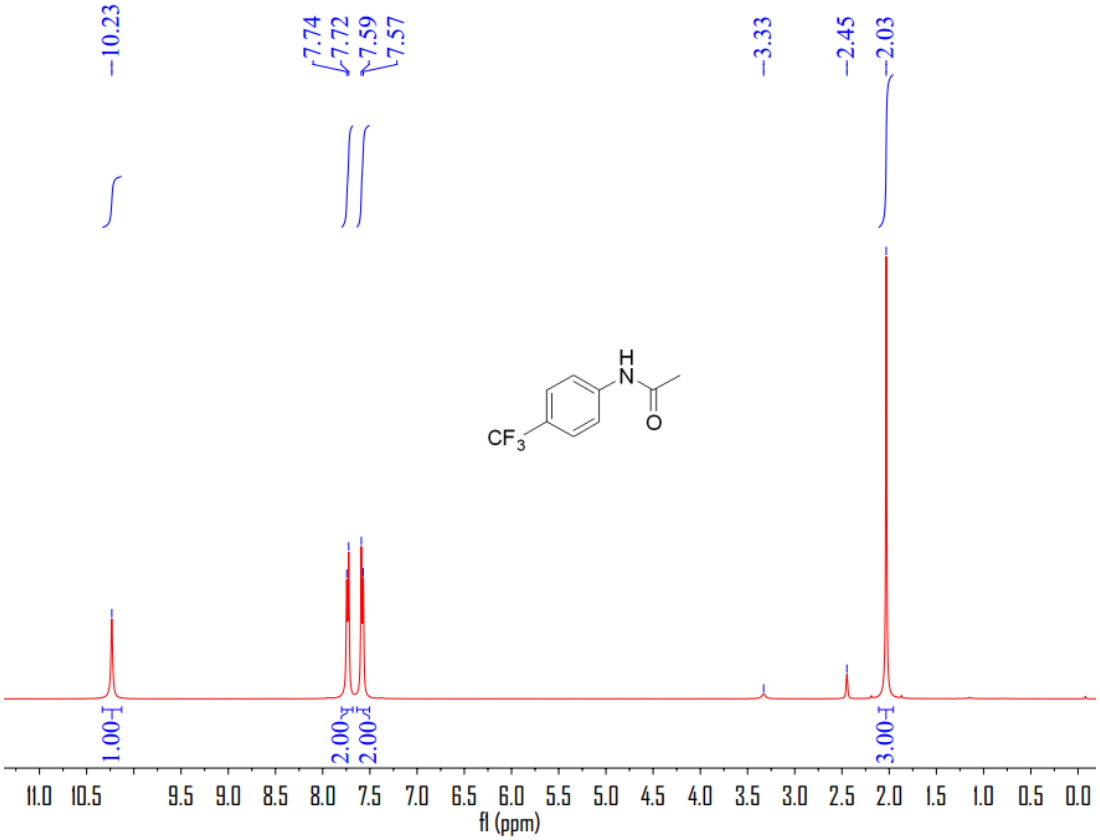
^{1}H NMR of **4j**



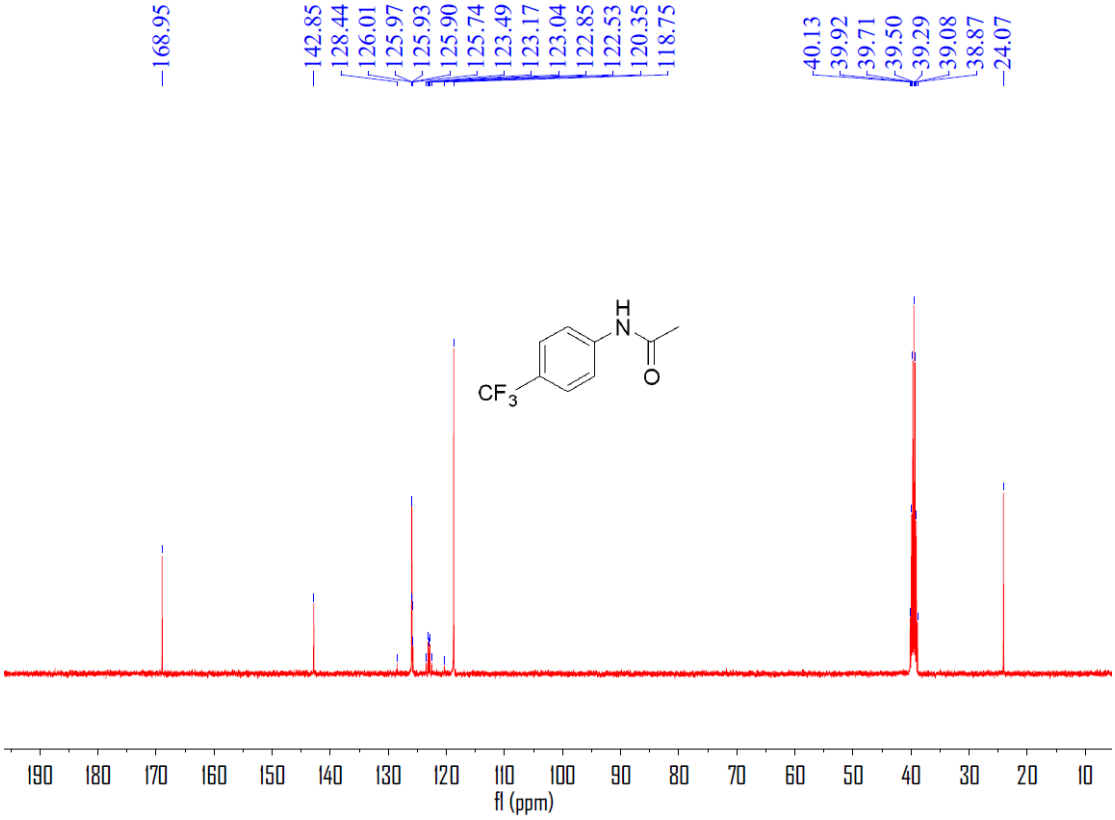
^{13}C NMR of **4j**



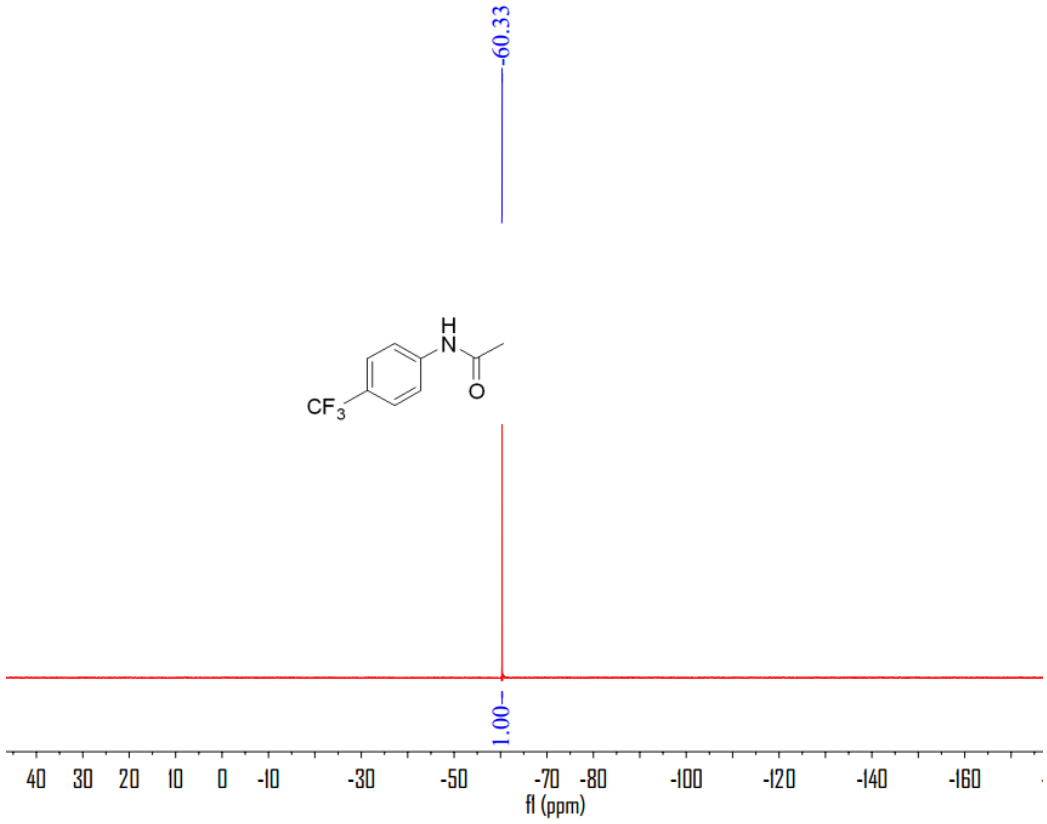
^{1}H NMR of **4k**



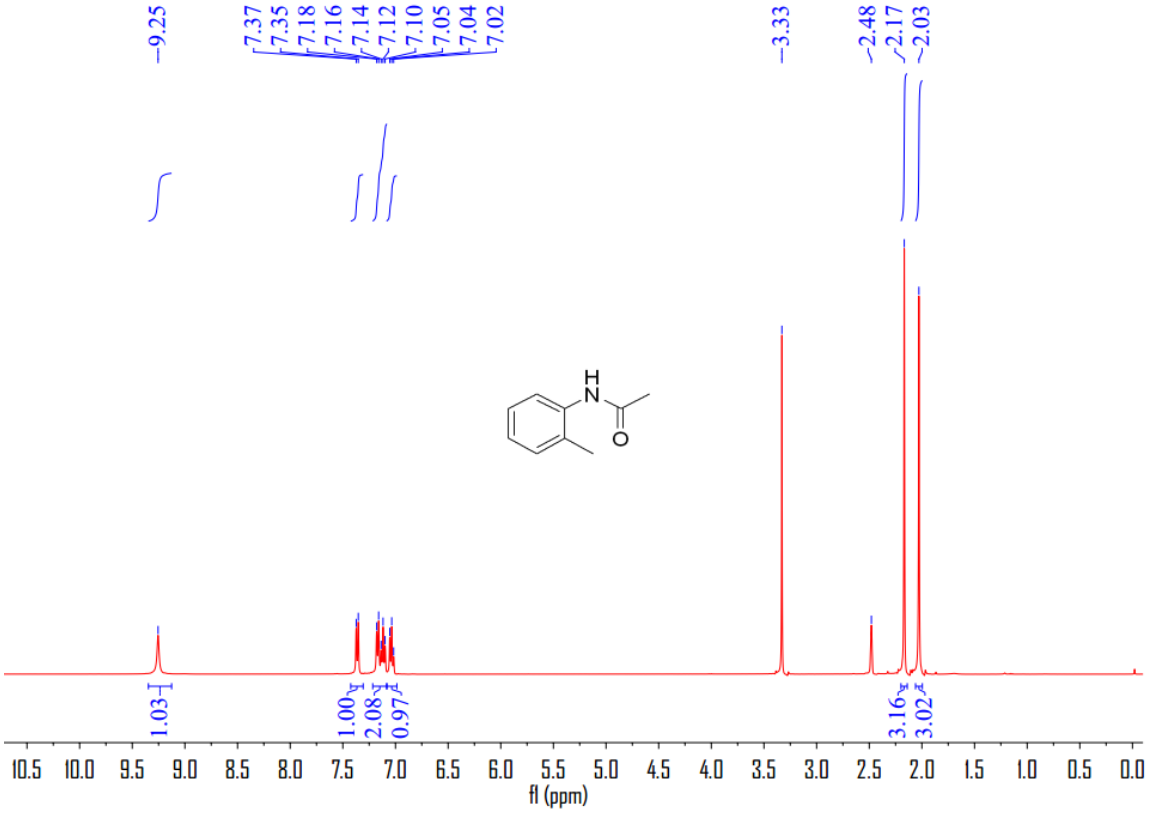
^{13}C NMR of **4k**



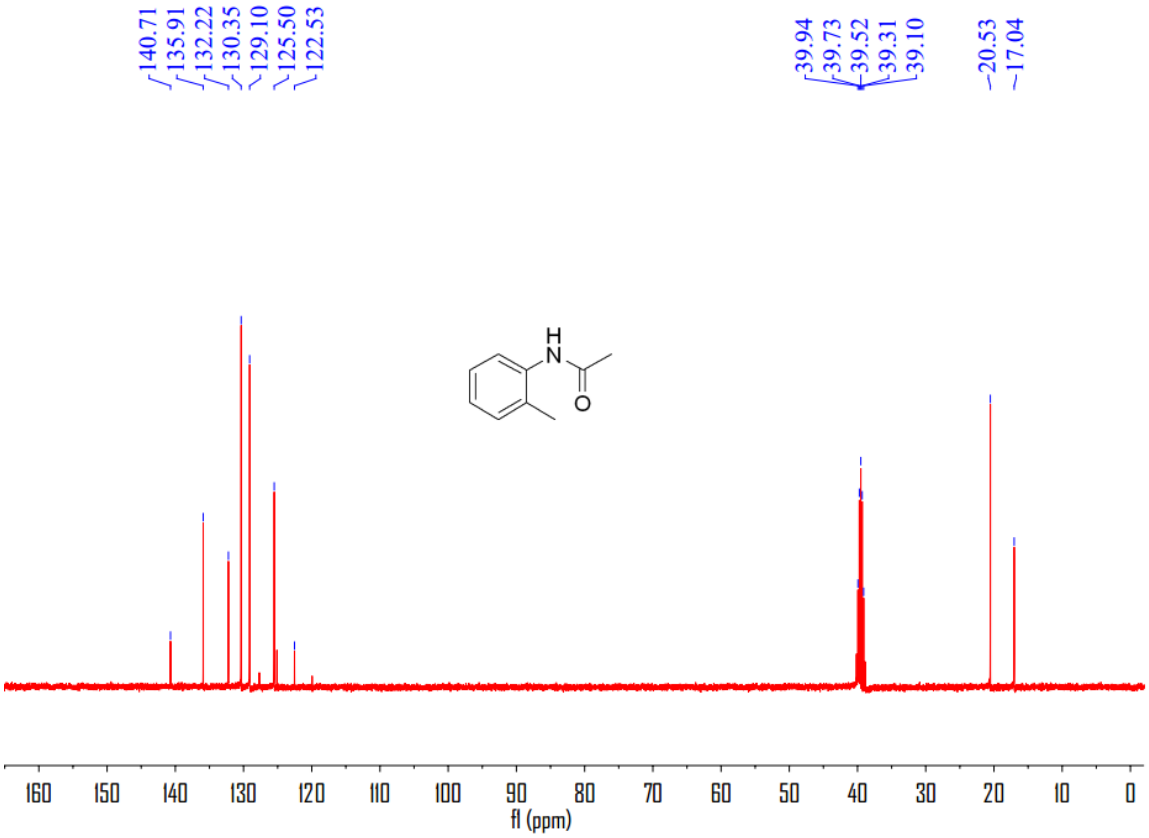
^{19}F NMR of **4k**



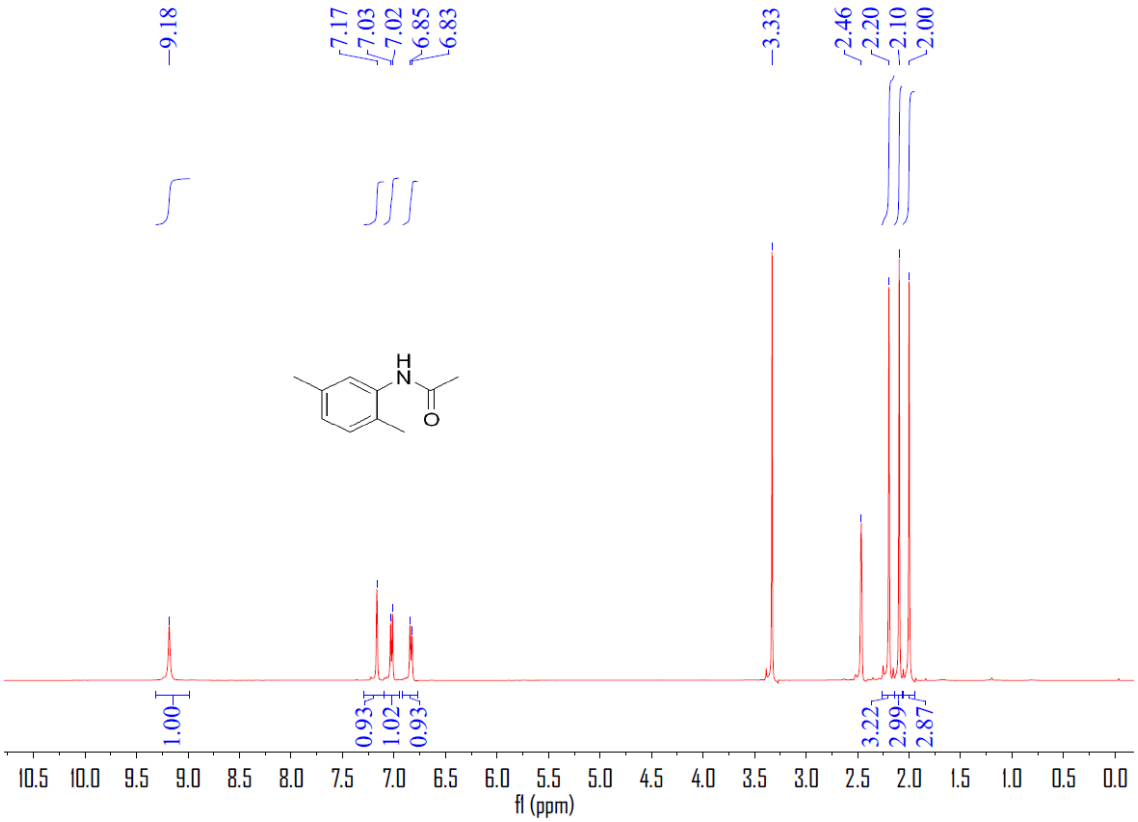
^{1}H NMR of **4l**



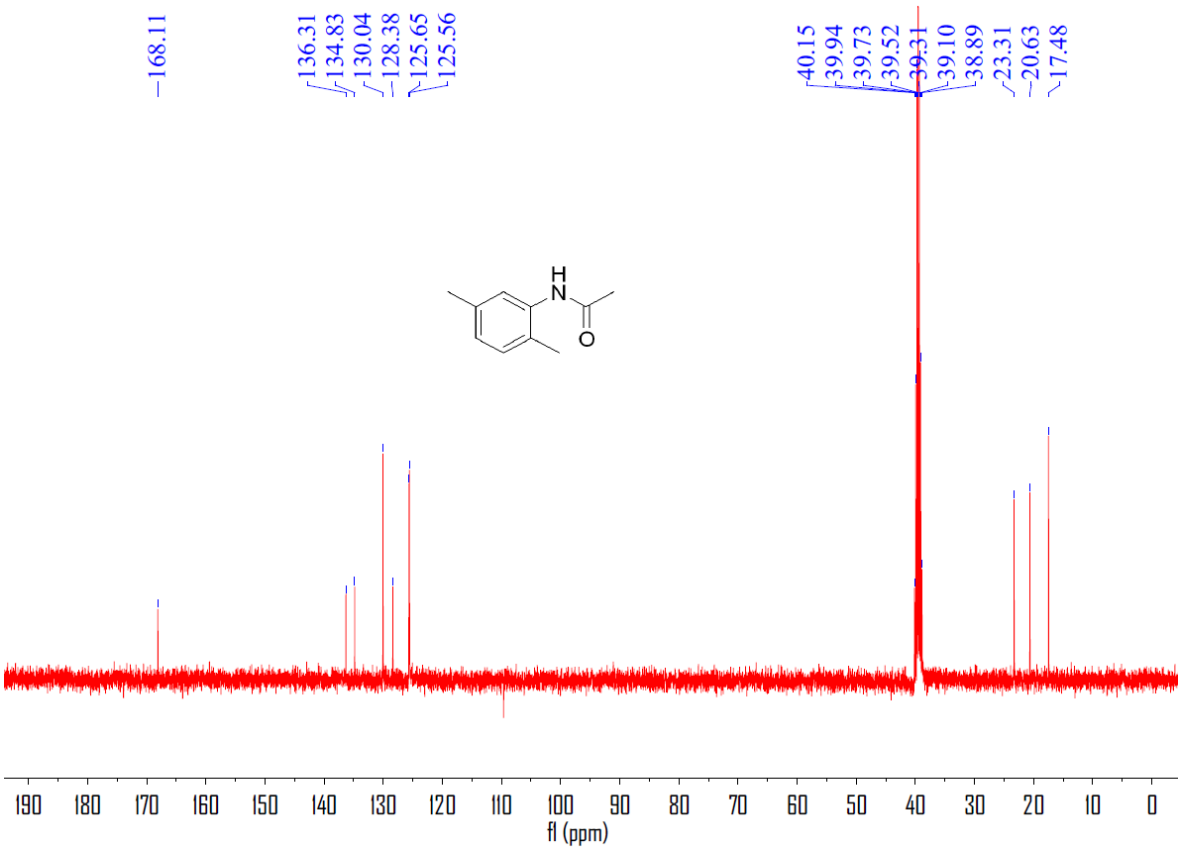
^{13}C NMR of **4l**



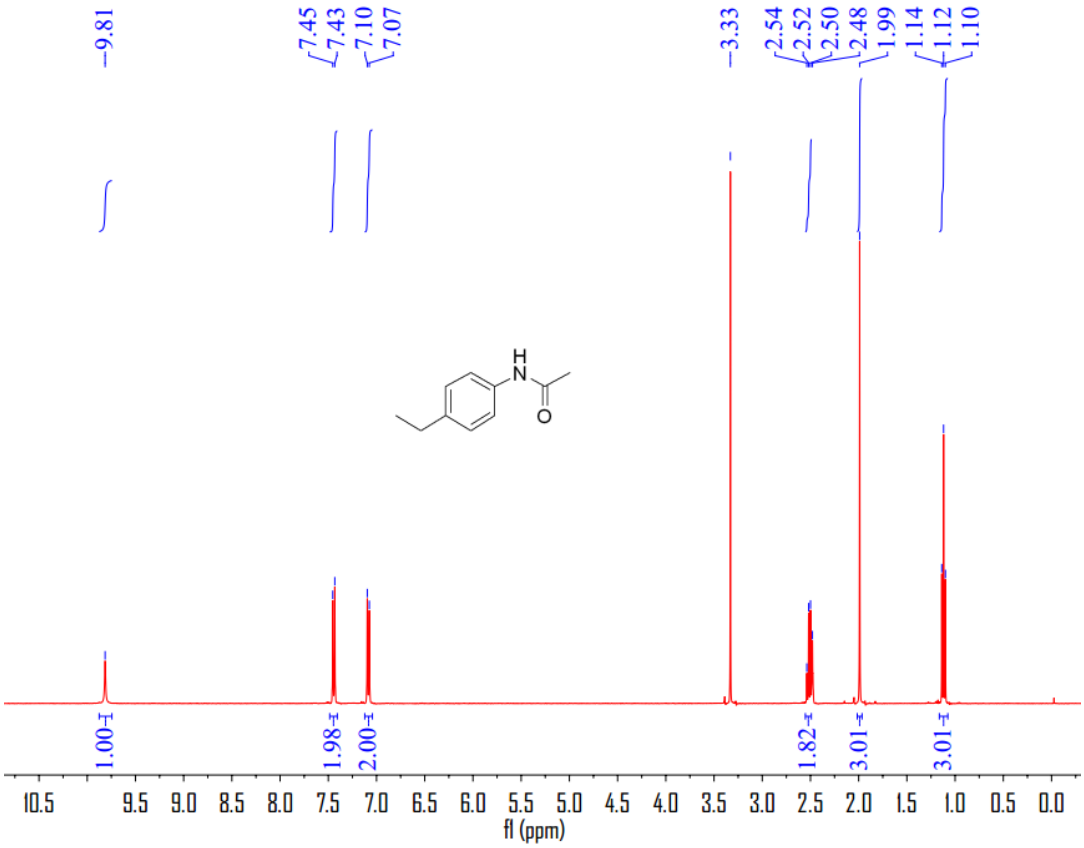
^{1}H NMR of **4m**



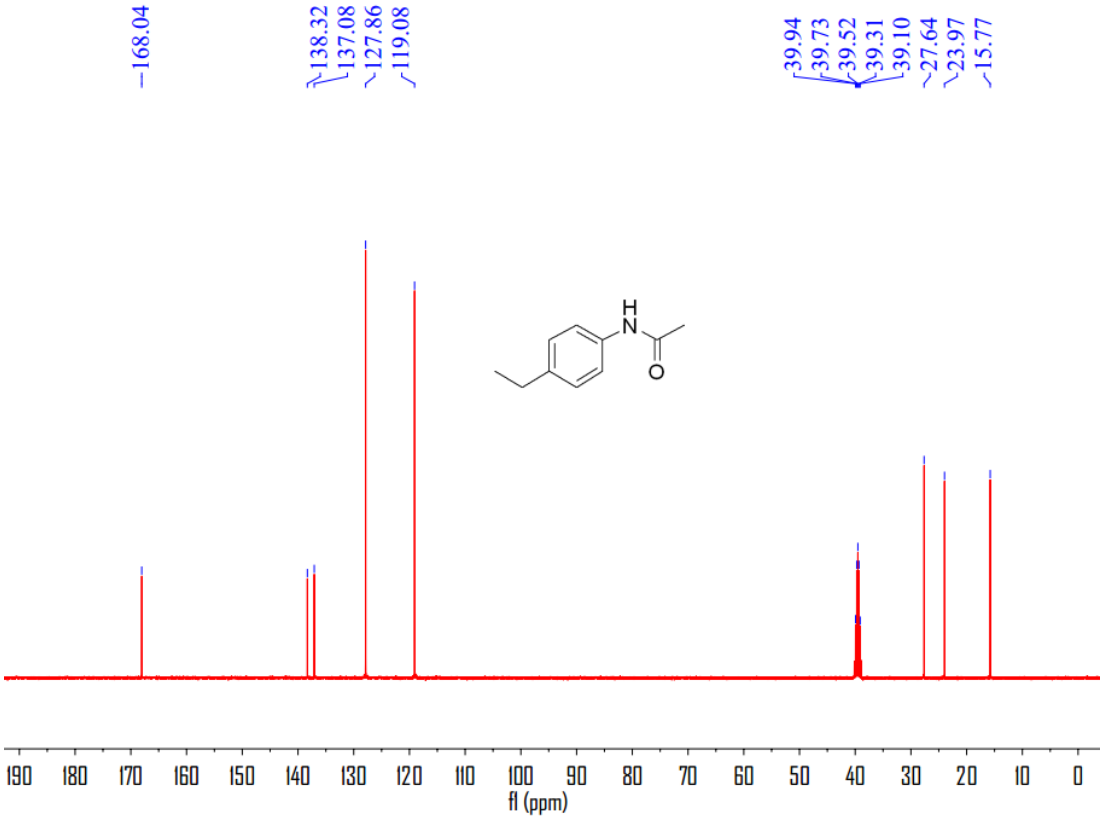
^{13}C NMR of **4m**



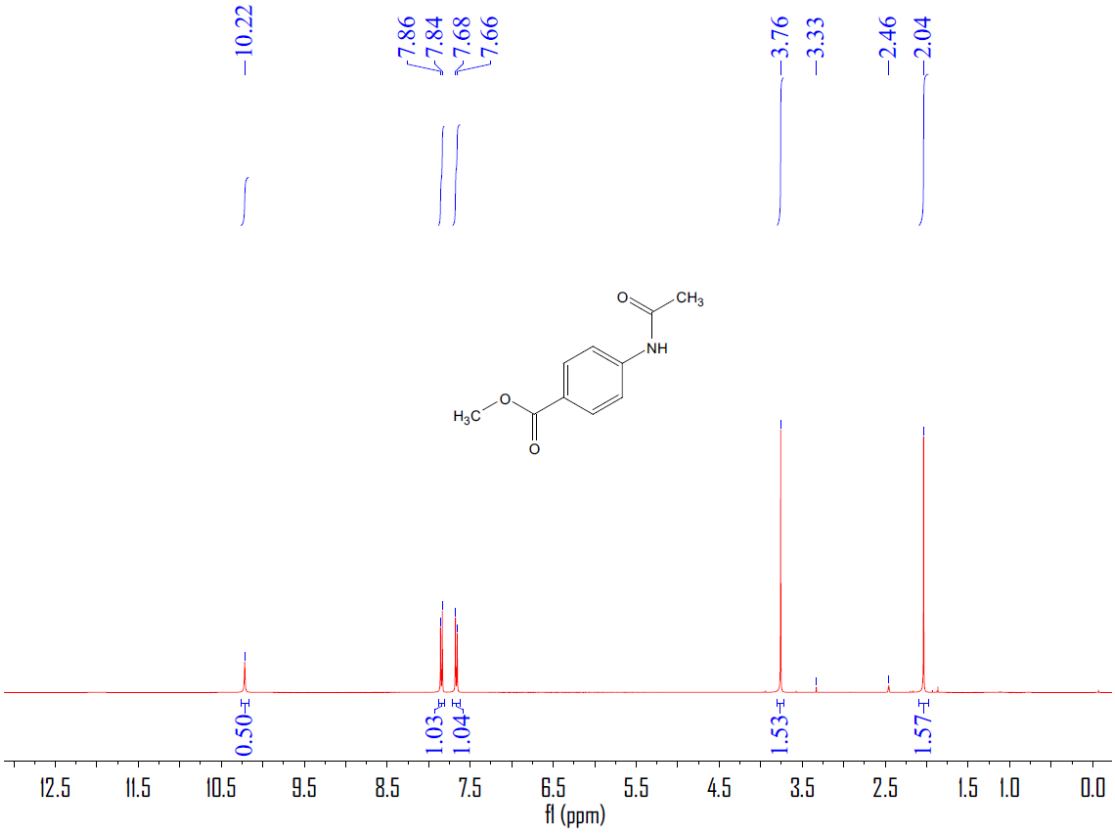
^{1}H NMR of **4n**



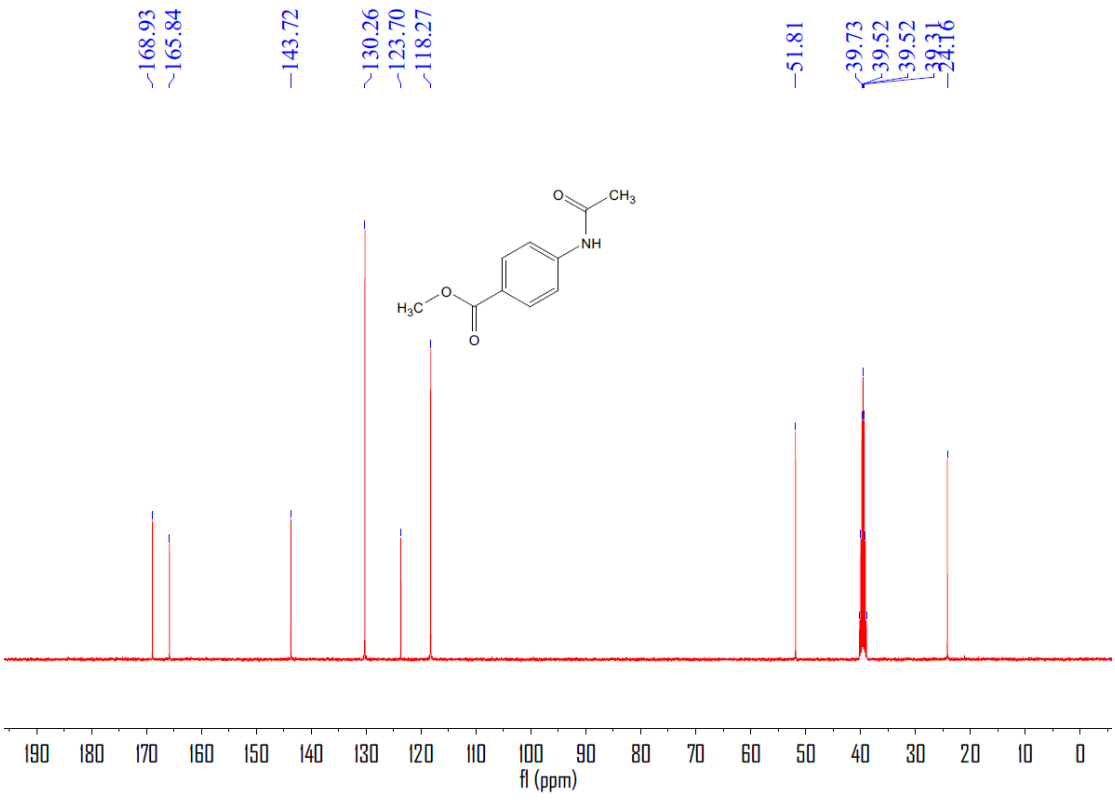
^{13}C NMR of **4n**



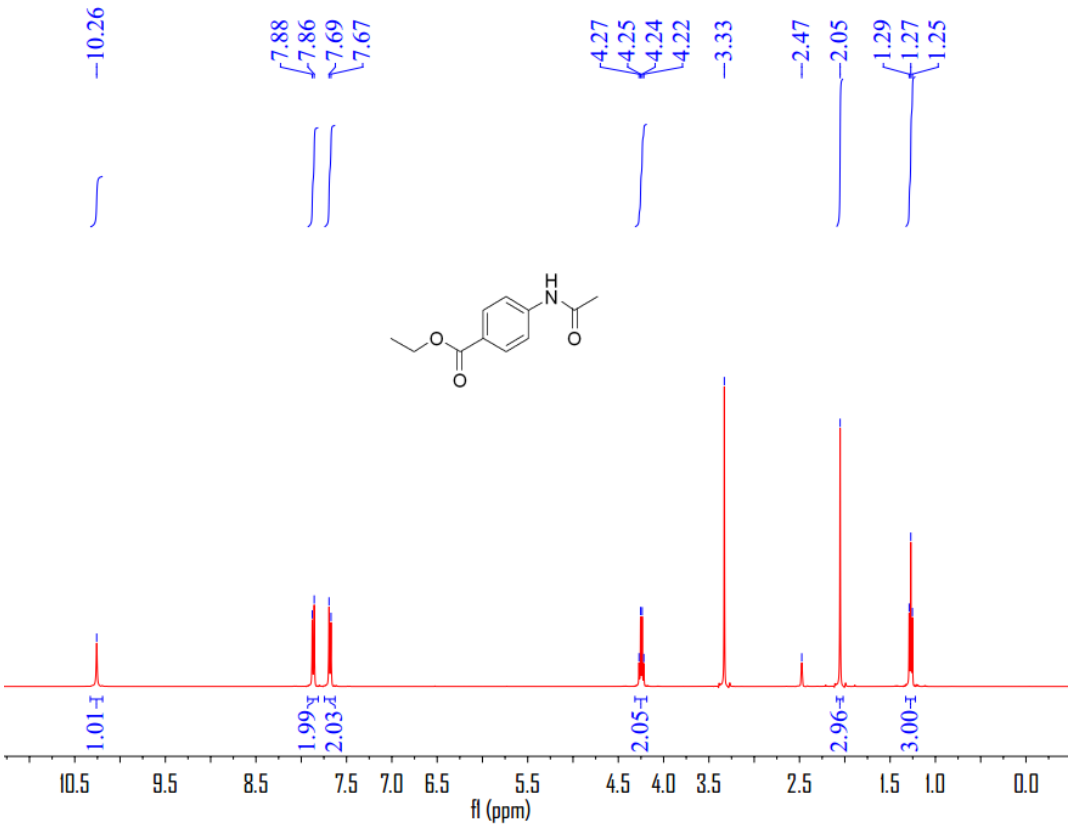
^{1}H NMR of **4o**



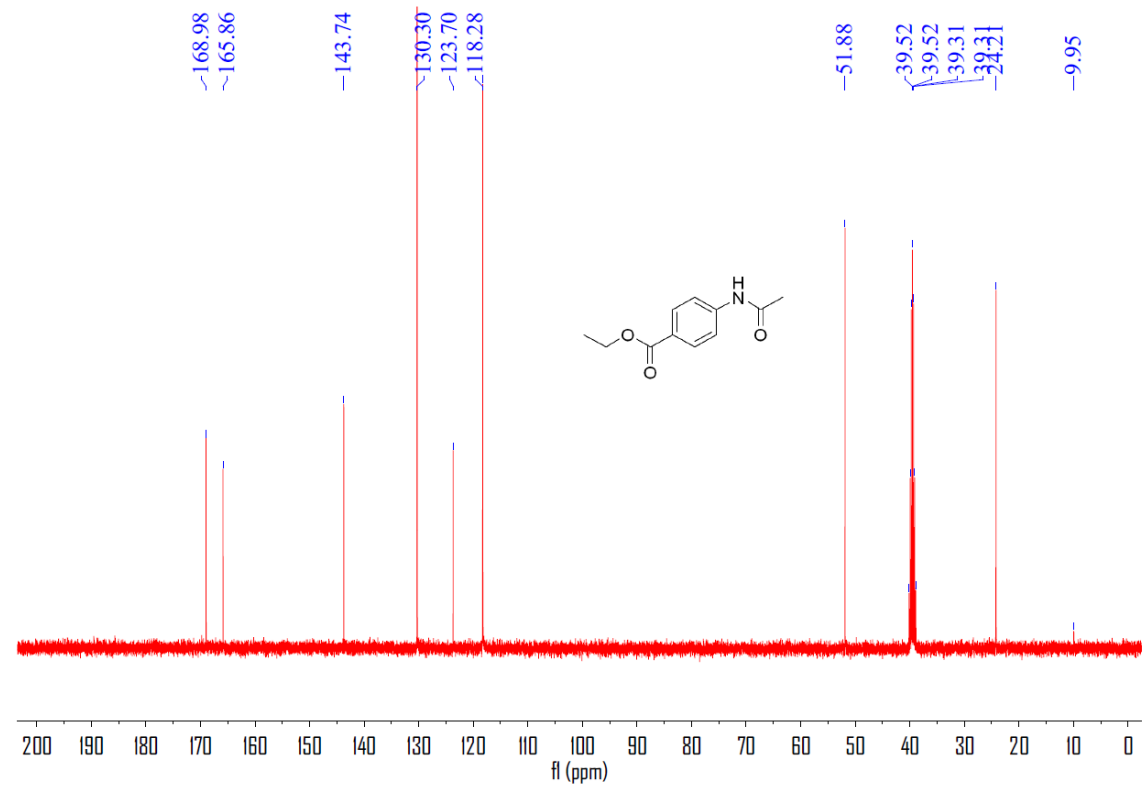
^{13}C NMR of **4o**



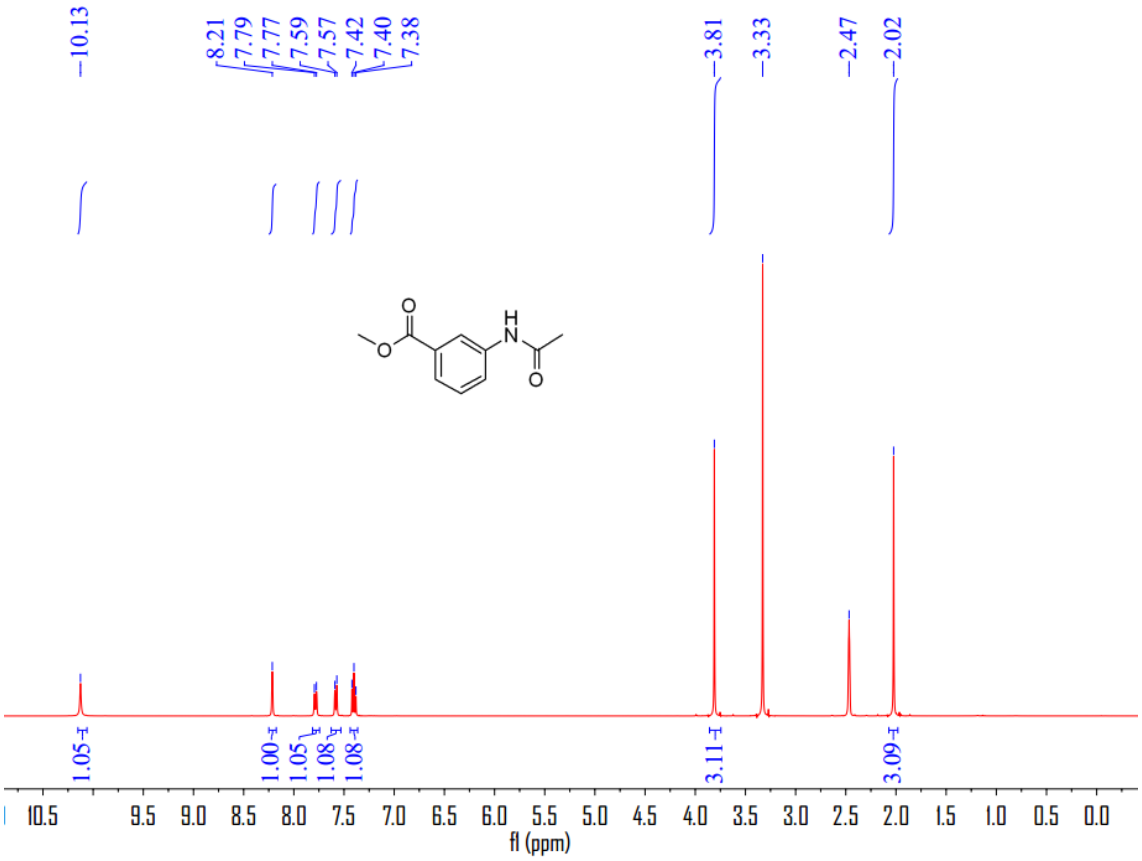
^{1}H NMR of **4p**



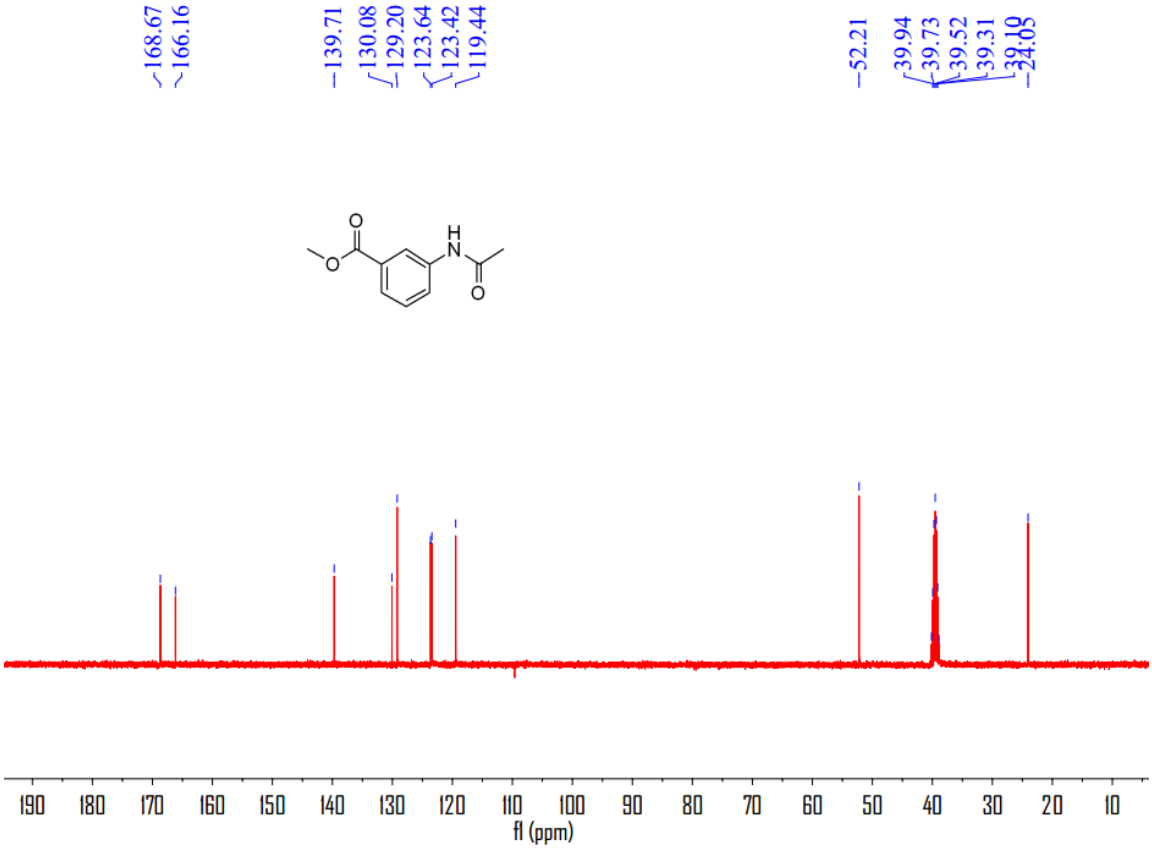
^{13}C NMR of **4p**



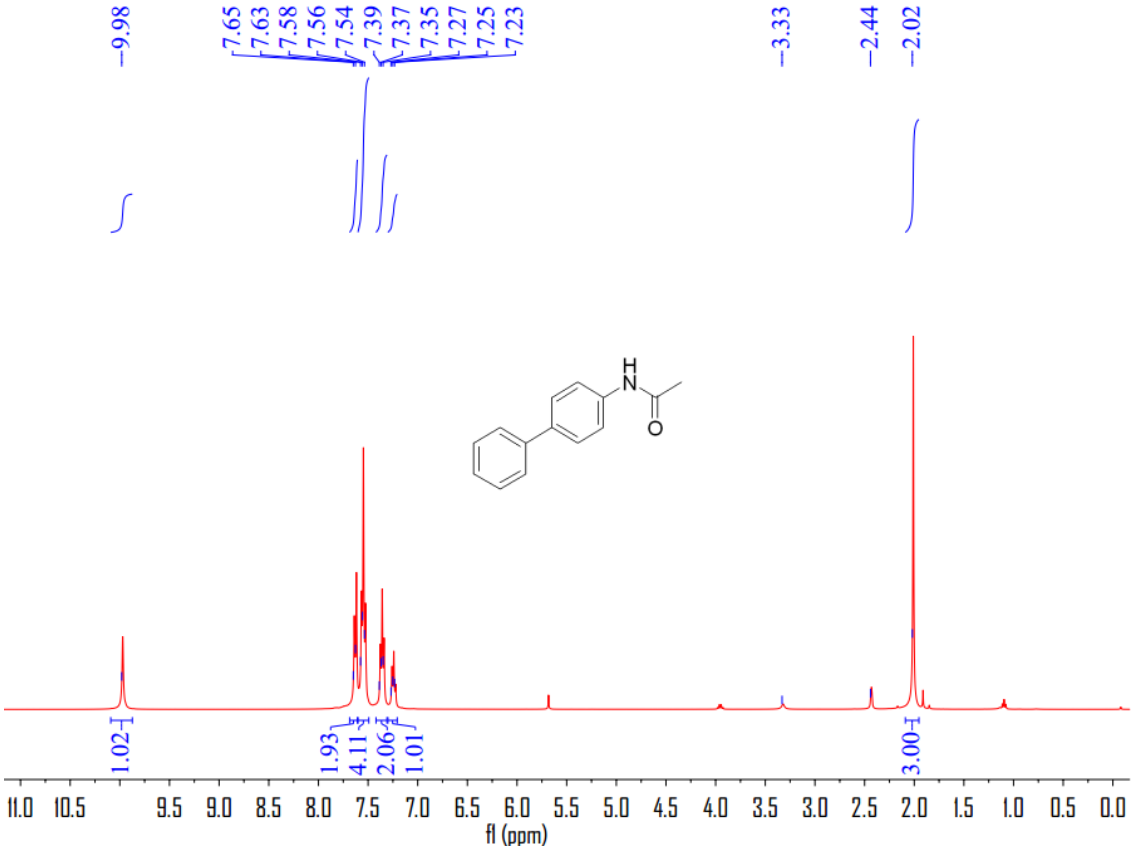
^{1}H NMR of **4q**


10.13
8.21
7.79
7.77
7.59
7.57
7.42
7.40
7.38
3.81
3.33
2.47
2.02
1.05
1.00
1.05
1.08
1.08
3.11
3.09
fl (ppm)

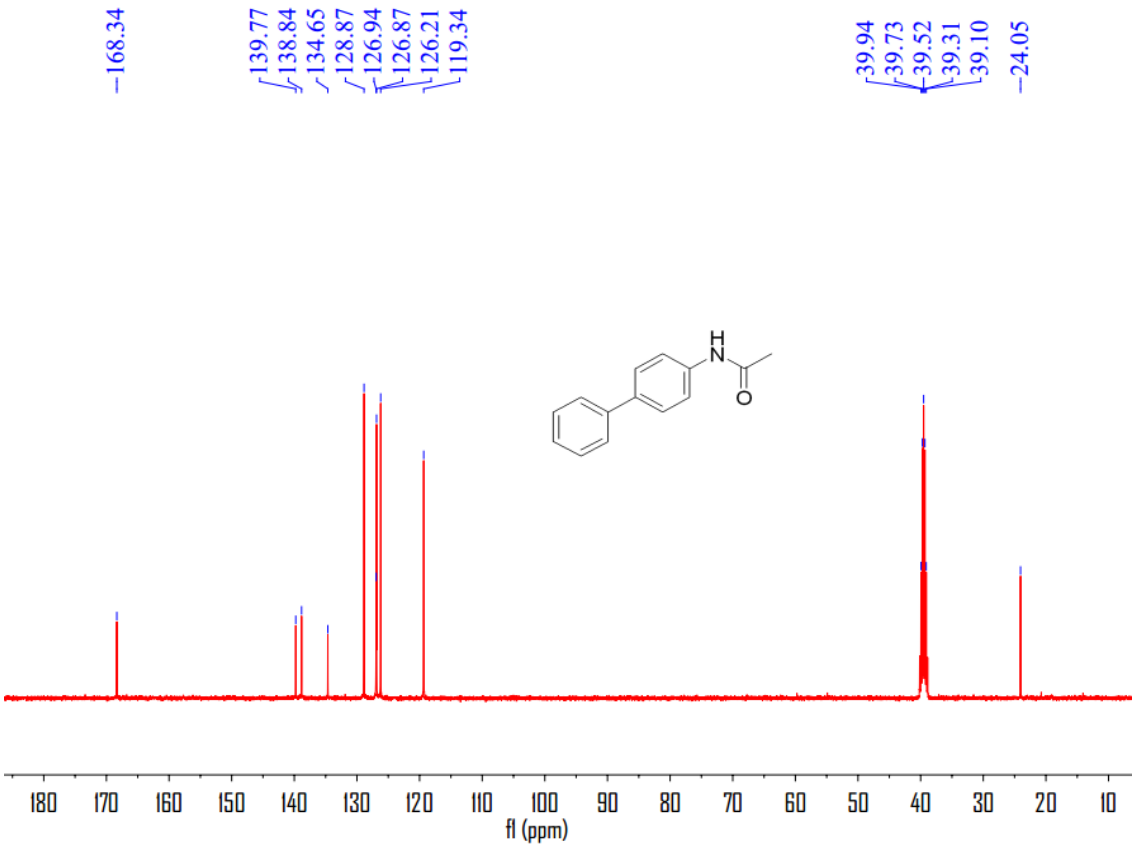
^{13}C NMR of **4q**


168.67
166.16
139.71
130.08
129.20
123.64
123.42
119.44
52.21
39.94
39.73
39.52
39.31
24.05
fl (ppm)

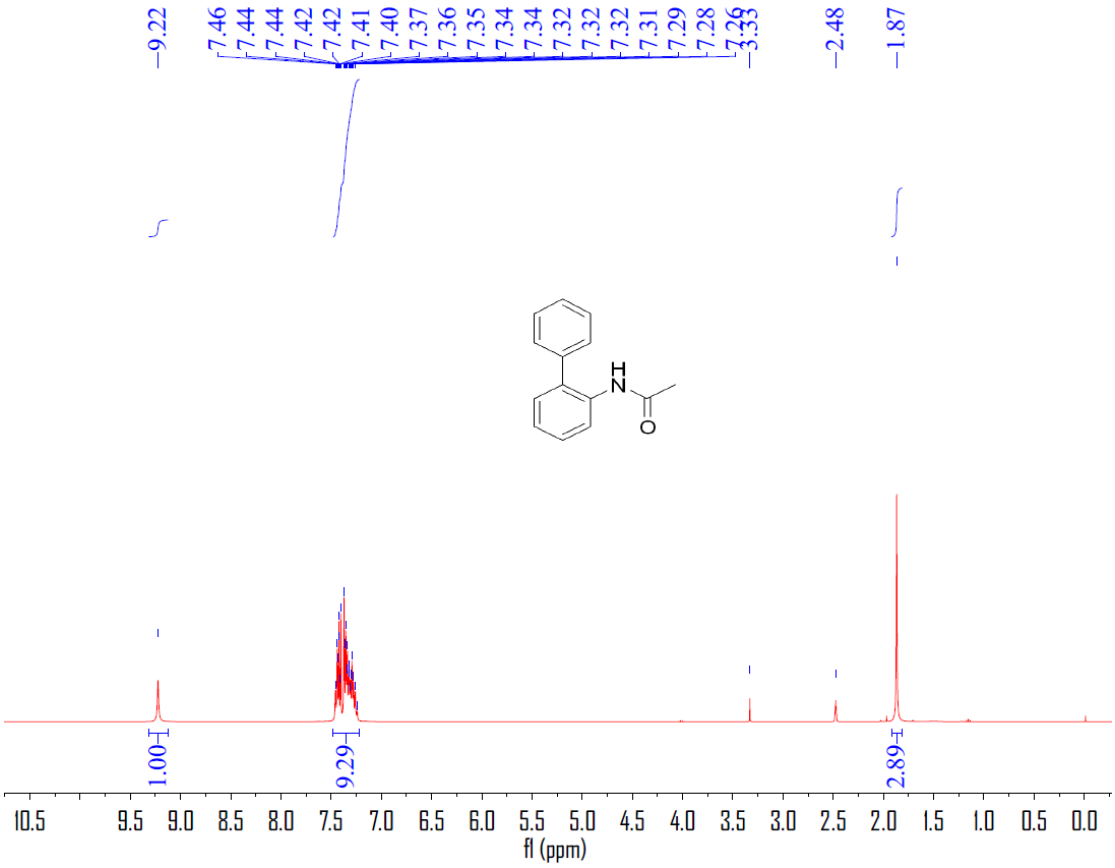
^{1}H NMR of **4r**



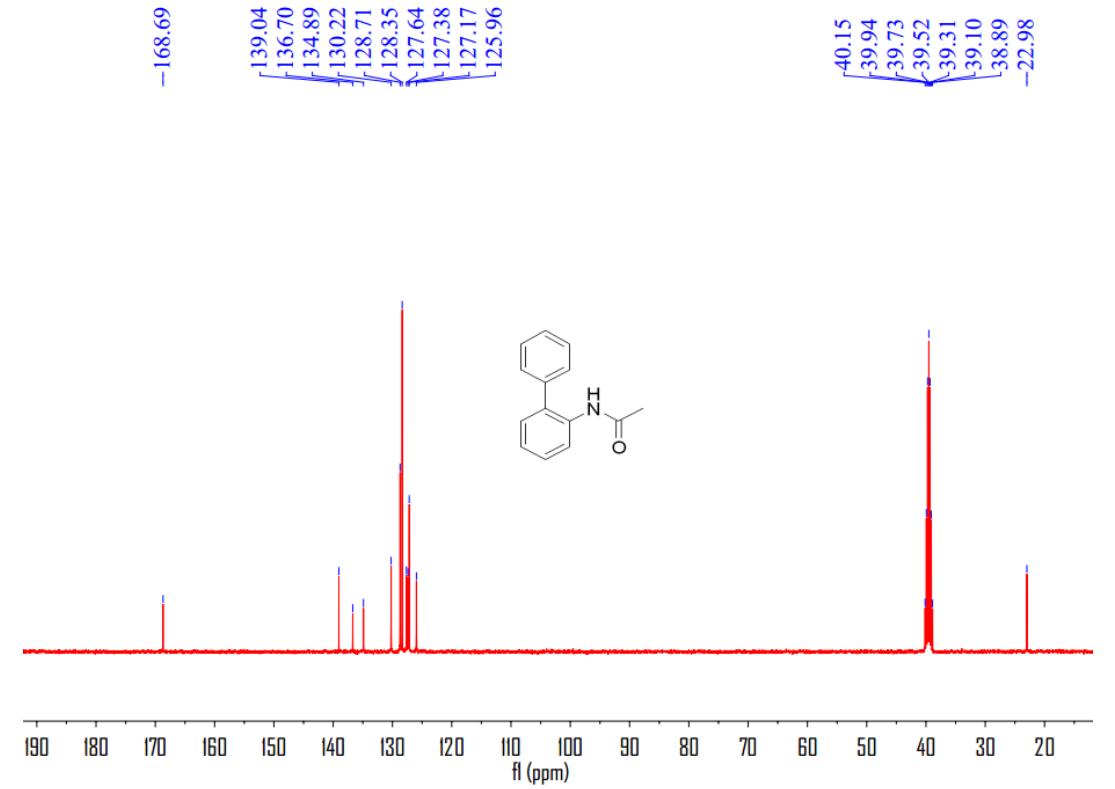
^{13}C NMR of **4r**



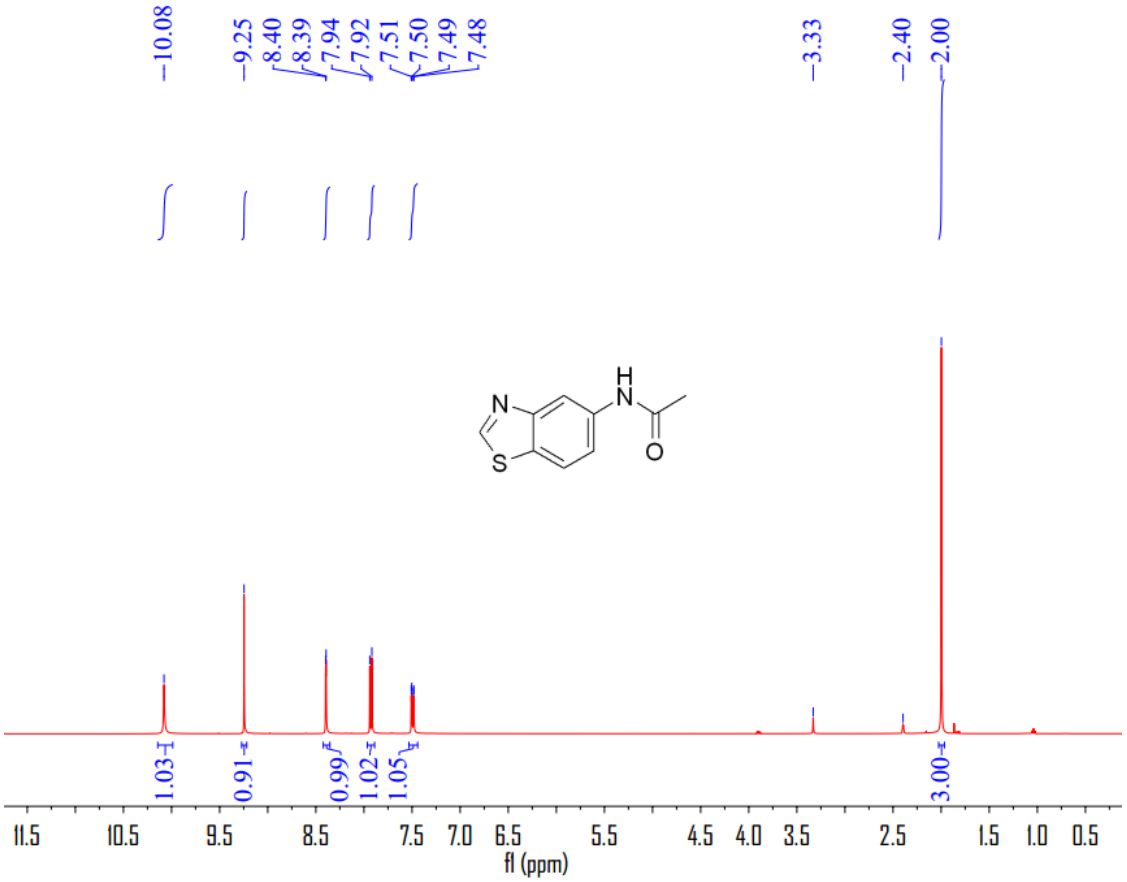
^{1}H NMR of **4s**



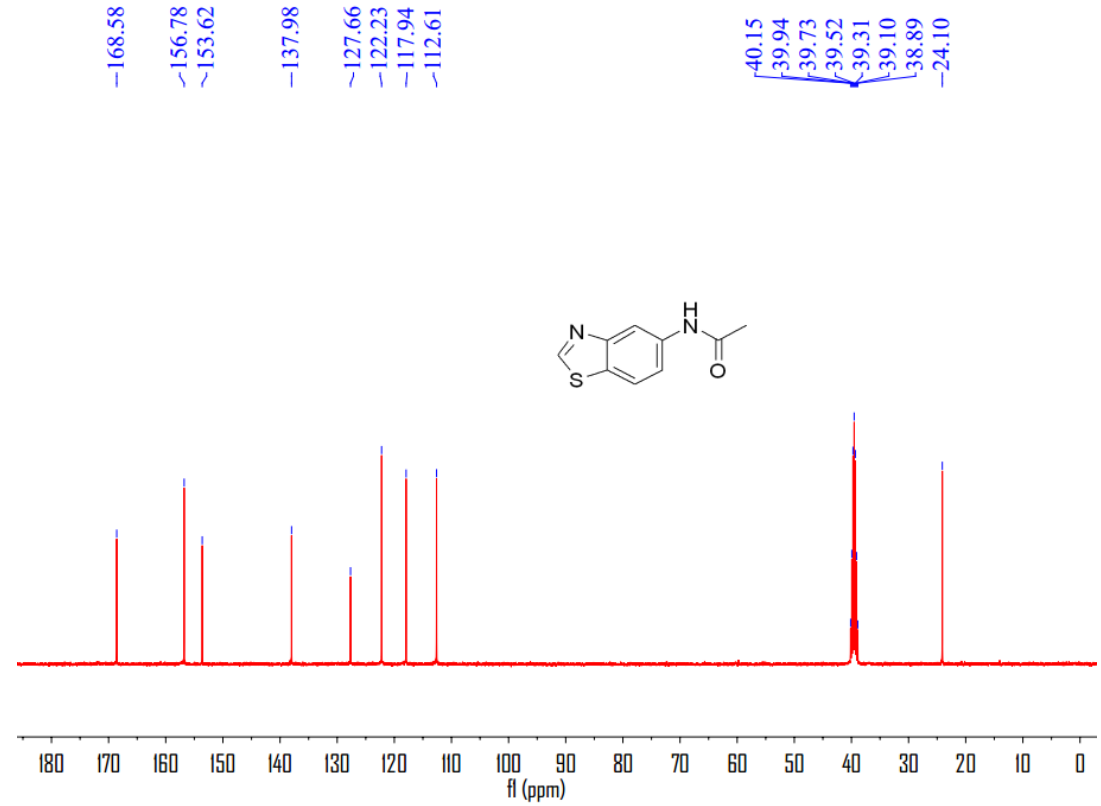
^{13}C NMR of **4s**



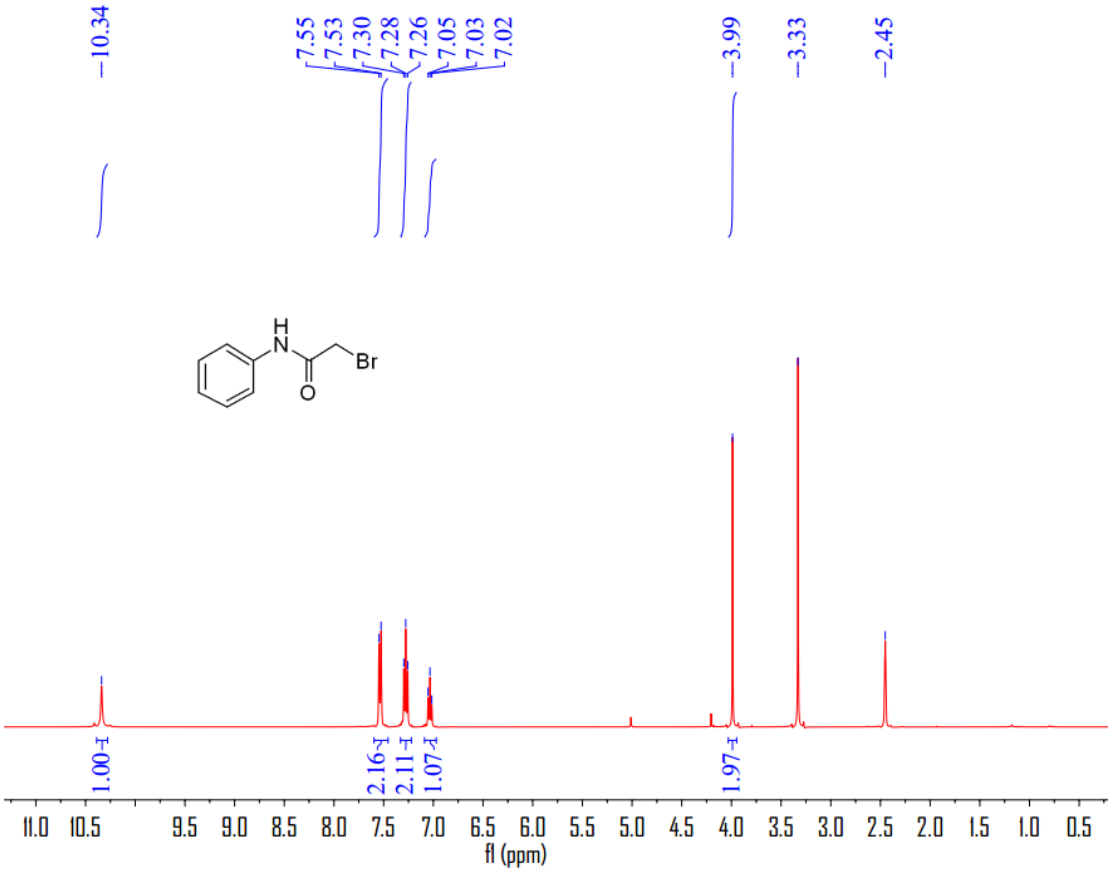
^{1}H NMR of **4t**



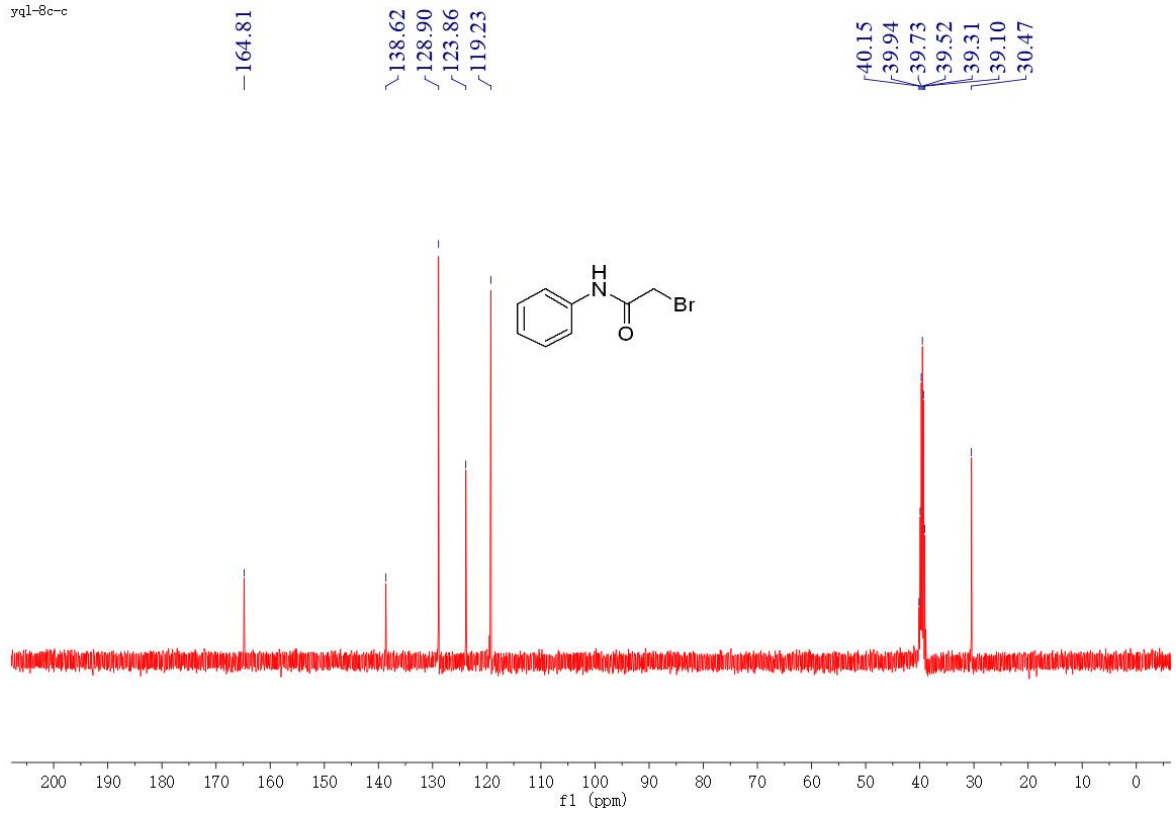
^{13}C NMR of **4t**



^{1}H NMR of **4u**



^{13}C NMR of **4u**



^{1}H NMR of **TEMPO-Ac**