
**Preparation of Highly Substituted (β -Acylamino)acrylates via
Iron-catalyzed Alkoxy carbonylation of *N*-Vinylacetamides with
Carbazates**

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Supporting Information

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1. General information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. ^1H -NMR and ^{13}C -NMR spectra were recorded at 25 °C on Bruker Advance 400M NMR spectrometers (CDCl_3 as solvent). Chemical shifts for ^1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of SiMe_4 (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) and etc. Coupling constants are reported as a J value in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform- d (δ 77.00 triplet). High resolution mass spectral analysis (HRMS) was performed on Waters-XEVOG2 Q-TOF (Waters Corporation). IR spectra were recorded on a commercial FT/IR spectrometer. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

2. Procedure for the synthesis of compound 3a - 3r.

To a stirred solution of **1** (0.3 mmol), **2** (0.6 mmol), Cs_2CO_3 (0.3 mmol) and $[\text{Fe}(\text{Pc})]$ (0.03 mmol) in MeCN (1.5 mL) was added TBHP (120 μL , 5-6 M in decane) slowly under an air atmosphere at room temperature. The mixture was heated at 60 °C for 2 h and then cooled to room temperature. The excess solvent was removed under vacuum, then the residue was directly purified by silica gel column chromatography (petroleum/ethyl acetate = 4:1) to give the desired product. The stereoselectivity (E/Z) was determined from the ^1H NMR spectra recorded for the crude products.

3. Procedure for the synthesis of compound 4a – 4l.

To a stirred solution of **1** (0.3 mmol), **2** (0.6 mmol), K_2CO_3 (0.3 mmol) and $[\text{Fe}(\text{Pc})]$ (0.03 mmol) in MeCN (1.5 mL) was added TBHP (120 μL , 5-6 M in decane) slowly under an air atmosphere at room temperature. The mixture was continued to react at

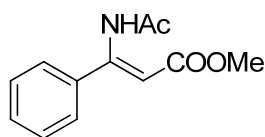
room temperature for 1 h. The excess solvent was removed under vacuum, and the residue was directly purified by silica gel column chromatography (petroleum/ethyl acetate = 4:1) to afford the desired product.

4. Procedure for the gram-scale synthesis of compound **3a**.

To a stirred solution of **1a** (1g, 6.2 mmol), **2a** (1.12g, 12.4 mmol), Cs₂CO₃ (2.02g, 0.3 mmol) and [Fe(Pc)] (0.35g, 0.62 mmol) in MeCN (30 mL) was added TBHP (2.48mL, 5-6 M in decane) slowly under an air atmosphere at room temperature. The mixture was heated at 60 °C for 2 h and then cooled to room temperature. The excess solvent was removed under vacuum, then the residue was directly purified by silica gel column chromatography (petroleum/ethyl acetate = 4:1) to give the desired product **3a** in 61% yield, 0.83g. The stereoselectivity (E/Z) was determined by the ¹H NMR spectra recorded for the crude product.

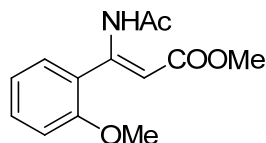
5. Characterization data for the products

(Z)-methyl 3-acetamido-3-phenylacrylate (**3a**)



3a^[2] was obtained as white solid. ¹H NMR (400 MHz, CDCl₃) δ 10.61 (s, 1H), 7.40 – 7.35 (m, 5H), 5.29 (s, 1H), 3.77 (s, 3H), 2.17 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 169.12, 168.51, 154.86, 135.97, 129.75, 128.18, 127.19, 100.67, 51.53, 24.92 ppm. HRMS (ESI): m/z calculated for C₁₂H₁₃NO₃ [M+Na]⁺: 242.0793, found: 242.0790. FTIR: 3289, 3059, 2950, 1723, 1678, 1624, 1289, 1174, 770, 697, 585, 517 cm⁻¹

(Z)-methyl 3-acetamido-3-(2-methoxyphenyl)acrylate (3b)

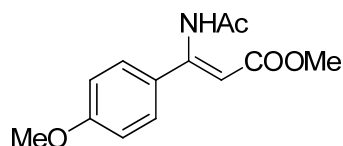


3b was obtained as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.92 (s, 1H), 7.35 (ddd, $J = 8.3, 7.5, 1.8$ Hz, 1H), 7.17 (dd, $J = 7.5, 1.8$ Hz, 1H), 6.95 (td, $J = 7.5, 1.0$ Hz, 1H), 6.85 (dd, $J = 8.3, 1.0$ Hz, 1H), 5.08 (s, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 169.56, 167.53, 156.83, 152.73, 130.63, 128.84, 125.74, 120.50, 110.35, 98.86, 55.74, 51.39, 24.81$ ppm.

HRMS (ESI): m/z calculated for $\text{C}_{13}\text{H}_{15}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 272.0899, found: 272.0893.

FTIR: 3263, 3078, 2958, 1728, 1667, 1625, 1491, 1302, 1194, 750, 588, 502 cm^{-1}

(Z)-methyl 3-acetamido-3-(4-methoxyphenyl)acrylate (3c)

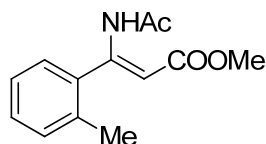


3c was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.56 (s, 1H), 7.33 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 5.27 (s, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) $\delta = 169.23, 168.74, 161.05, 154.51, 128.79, 128.03, 113.65, 99.62, 55.41, 51.44, 25.03$ ppm.

HRMS (ESI): m/z calculated for $\text{C}_{13}\text{H}_{15}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 272.0899, found: 272.0895.

FTIR: 3332, 2969, 2833, 1682, 1624, 1508, 1286, 1165, 1026, 823, 560, 489 cm^{-1}

(Z)-methyl 3-acetamido-3-(o-tolyl)acrylate (3d)



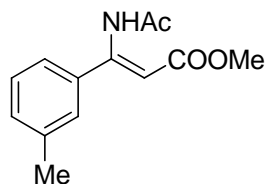
3d was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 11.03 (s, 1H), 7.29–7.25 (m, 1H), 7.22–7.09 (m, 3H), 5.01 (s, 1H), 3.77 (s, 3H), 2.26 (s, 3H), 2.10 (s,

3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 169.53, 167.52, 155.00, 136.21, 135.23, 129.76, 128.82, 127.48, 125.61, 98.83, 51.44, 24.73, 19.54 ppm.

HRMS (ESI): m/z calculated for $\text{C}_{13}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{Na}]^+$: 256.0950, found: 256.0952.

FTIR: 3278, 3063, 2951, 1727, 1677, 1620, 1487, 1295, 1175, 770, 602, 585, 472 cm^{-1}

(Z)-methyl 3-acetamido-3-(m-tolyl)acrylate (3e)

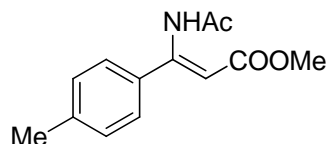


3e was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.57 (s, 1H), 7.32 – 7.13 (m, 4H), 5.28 (s, 1H), 3.76 (s, 3H), 2.36 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 169.15, 168.54, 155.03, 137.88, 135.93, 130.60, 128.05, 127.73, 124.39, 100.56, 51.51, 24.93, 21.55 ppm.

HRMS (ESI): m/z calculated for $\text{C}_{13}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{Na}]^+$: 256.0950, found: 219.0948.

FTIR: 3289, 3059, 2950, 1723, 1678, 1624, 1289, 1174, 770, 697, 585, 517 cm^{-1}

(Z)-methyl 3-acetamido-3-(p-tolyl)acrylate (3f)

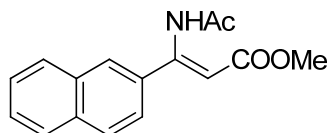


3f was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.57 (s, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 5.28 (s, 1H), 3.76 (s, 3H), 2.37 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 169.16, 168.60, 154.88, 139.99, 133.00, 128.92, 127.14, 100.16, 51.46, 24.94, 21.50 ppm.

HRMS (ESI): m/z calculated for $\text{C}_{13}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{Na}]^+$: 256.0950, found: 256.0944.

FTIR: 3263, 3078, 2958, 1728, 1667, 1625, 1491, 1275, 1022, 750, 588, 502 cm^{-1}

(Z)-methyl 3-acetamido-3-(naphthalen-2-yl)acrylate (3g)

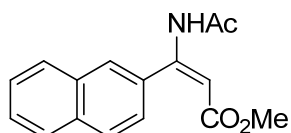


3g was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.71 (s, 1H), 7.94 – 7.77 (m, 4H), 7.57 – 7.40 (m, 3H), 5.41 (s, 1H), 3.79 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 169.17, 168.60, 154.86, 134.00, 133.70, 133.00, 128.63, 127.85, 127.57, 127.02, 126.53, 124.93, 100.91, 51.60, 24.94 ppm.

HRMS (ESI): m/z calculated for $\text{C}_{16}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{Na}]^+$: 292.0950, found: 292.0950.

FTIR: 3277, 3057, 2922, 1722, 1674, 1617, 1286, 1167, 818, 745, 480 cm^{-1} .

(E)-methyl 3-acetamido-3-(naphthalen-2-yl)acrylate (**3g'**)

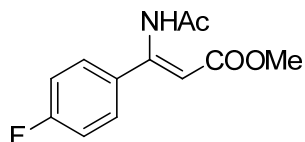


3g' obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.86 (t, J = 6.5 Hz, 3H), 7.79 (s, 1H), 7.58 – 7.48 (m, 2H), 7.40 (dd, J = 8.5, 1.8 Hz, 1H), 7.15 (s, 1H), 6.88 (s, 1H), 3.52 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 169.02, 167.72, 149.19, 134.15, 133.65, 133.01, 128.39, 128.19, 127.99, 127.15, 127.13, 126.73, 126.15, 103.88, 51.16, 25.14 ppm.

HRMS (ESI): m/z calculated for $\text{C}_{16}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{Na}]^+$: 292.0950, found: 292.0952.

FTIR: 3276, 3135, 2947, 1716, 1678, 1513, 1284, 1142, 820, 747, 474 cm^{-1} .

(Z)-methyl 3-acetamido-3-(4-fluorophenyl)acrylate (**3h**)

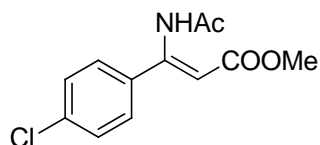


3h was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.62 (s, 1H), 7.48 – 7.30 (m, 2H), 7.04 (t, J = 8.6 Hz, 2H), 5.25 (s, 1H), 3.77 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 169.03, 168.58, 163.66 (d, J = 249 Hz), 153.73, 131.92 (d, J = 4 Hz), 129.16 (d, J = 9 Hz), 115.31 (d, J = 22 Hz), 100.66, 51.59, 24.95 ppm.

HRMS (ESI): m/z calculated for $C_{12}H_{12}FNO_3$ $[M+Na]^+$: 260.0699, found: 260.0694.

FTIR: 3263, 3044, 2956, 1724, 1623, 1509, 1295, 1172, 844, 779, 544 cm^{-1}

(Z)-methyl 3-acetamido-3-(4-chlorophenyl)acrylate (**3i**)

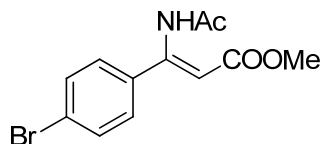


3i was obtained as white solid. 1H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.33 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 5.26 (s, 1H), 3.76 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.93, 168.53, 153.54, 135.73, 134.38, 128.49, 128.45, 100.93, 51.61, 24.87 ppm.

HRMS (ESI): m/z calculated for $C_{12}H_{12}ClNO_3$ $[M+Na]^+$: 276.0403, found: 276.0401.

FTIR: 3270, 2952, 1723, 1673, 1624, 1491, 1290, 1177, 813, 529, 474 cm^{-1}

(Z)-methyl 3-acetamido-3-(4-bromophenyl)acrylate (**3j**)

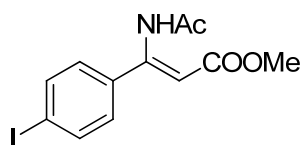


3j was obtained as white solid. 1H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 5.26 (s, 1H), 3.77 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.94, 168.55, 153.62, 134.88, 131.43, 128.74, 124.05, 100.95, 51.64, 24.89 ppm.

HRMS (ESI): m/z calculated for $C_{12}H_{12}BrNO_3$ $[M+Na]^+$: 319.9898, found: 319.9898

FTIR: 3286, 2950, 1723, 1681, 1622, 1488, 1288, 1176, 820, 717, 522 cm^{-1}

(Z)-methyl 3-acetamido-3-(4-iodophenyl)acrylate (**3k**)



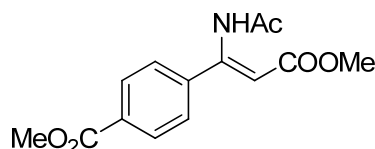
3k was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.59 (s, 0H), 7.69 (d, $J = 8.5$ Hz, 1H), 7.10 (d, $J = 8.3$ Hz, 1H), 5.26 (s, 0H), 3.76 (d, $J = 2.2$ Hz, 1H), 2.16 (d, $J = 2.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 168.94, 168.54, 153.74, 137.36, 135.51, 128.82, 100.96, 95.99, 51.65, 24.88$ ppm.

HRMS (ESI): m/z calculated for $\text{C}_{12}\text{H}_{12}\text{INO}_3$ $[\text{M}+\text{Na}]^+$: 367.9760, found: 367.9758

FTIR: 3435, 3242, 2957, 1727, 1673, 1619, 1848, 1288, 1176, 816, 697, 520, 467 cm^{-1}

(Z)-methyl 4-(1-acetamido-3-methoxy-3-oxoprop-1-en-1-yl)benzoate

(3l)

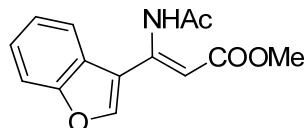


3l was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.63 (s, 1H), 8.02 (d, $J = 8.3$ Hz, 2H), 7.42 (d, $J = 8.3$ Hz, 2H), 5.30 (s, 1H), 3.91 (s, 3H), 3.77 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 168.87, 168.46, 166.62, 153.64, 140.49, 131.02, 129.48, 127.16, 101.59, 52.34, 51.69, 24.79$ ppm.

HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{15}\text{NO}_5$ $[\text{M}+\text{Na}]^+$: 300.0848, found: 300.0847.

FTIR: 3326, 2953, 1710, 1680, 1628, 1501, 1432, 1285, 1172, 1109, 855, 776, 709, 566 cm^{-1}

(Z)-methyl 3-acetamido-3-(benzofuran-3-yl)acrylate (3m)

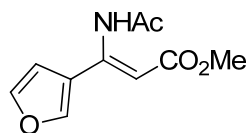


3m was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.15 (s, 1H), 7.58 (d, $J = 7.7$ Hz, 1H), 7.46 (d, $J = 8.3$ Hz, 1H), 7.33 (t, $J = 7.5$ Hz, 1H), 7.23 (t, $J = 7.5$ Hz, 1H), 7.08 (s, 1H), 5.92 (s, 1H), 3.78 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 168.75, 168.74, 155.02, 149.67, 142.47, 128.00, 126.10, 123.29, 121.93, 111.46, 109.77, 101.27, 51.64, 24.59$ ppm.

HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{13}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 282.0742, found: 282.0739.

FTIR: 3293, 3014, 2946, 1711, 1692, 1630, 1556, 1283, 1217, 816, 755, 628, 512 cm^{-1}

(Z)-methyl 3-acetamido-3-(furan-3-yl)acrylate (3n)

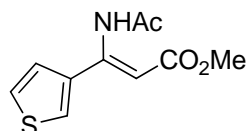


3n was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.28 (s, 1H), 7.39 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.27 (dd, $J = 3.6, 1.3$ Hz, 1H), 7.02 (dd, $J = 5.0, 3.7$ Hz, 1H), 5.52 (s, 1H), 3.76 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 169.03, 168.78, 147.38, 137.74, 128.58, 128.10, 127.38, 100.89, 51.59, 24.90$ ppm.

HRMS (ESI): m/z calculated for $\text{C}_{10}\text{H}_{11}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 232.0586, found: 232.0583.

FTIR: 3290, 3101, 2949, 1681, 1616, 1510, 1273, 1171, 1042, 827, 710 cm^{-1}

(Z)-methyl 3-acetamido-3-(thiophen-3-yl)acrylate (3o)

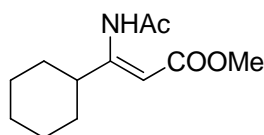


3o was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.17 (s, 1H), 7.46 (d, $J = 1.8$ Hz, 1H), 6.75 (d, $J = 3.5$ Hz, 1H), 6.46 (dd, $J = 3.3, 1.8$ Hz, 1H), 5.68 (s, 1H), 3.75 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 169.22, 168.78, 148.08, 144.23, 142.54, 113.93, 112.02, 98.73, 51.61, 24.77$ ppm.

HRMS (ESI): m/z calculated for $\text{C}_{10}\text{H}_{11}\text{NO}_3\text{S}$ $[\text{M}+\text{Na}]^+$: 248.0357, found: 248.0358.

FTIR: 3303, 3143, 2951, 1718, 1629, 1475, 1289, 1199, 822, 748, 592, 504 cm^{-1}

(Z)-methyl 3-acetamido-3-cyclohexylacrylate (3p)

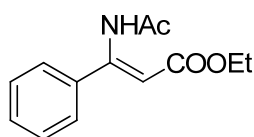


3p was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 11.10 (s, 1H), 5.01 (s, 1H), 3.67 (s, 3H), 3.58 – 3.40 (m, 1H), 2.11 (s, 3H), 1.90 – 1.86 (m, 2H), 1.80 – 1.65 (m, 3H), 1.40 – 1.31 (m, 2H), 1.21 – 1.02 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 170.22, 168.52, 164.68, 92.69, 51.16, 39.41, 32.18, 26.40, 26.30, 25.72 ppm.

HRMS (ESI): m/z calculated for $\text{C}_{12}\text{H}_{19}\text{NO}_3$ $[\text{M}+\text{Na}]^+$: 248.1263, found: 248.1260.

FTIR: 3429, 2927, 2853, 1717, 1674, 1628, 1493, 1250, 1222, 1165, 814, 670 cm^{-1}

(Z)-ethyl 3-acetamido-3-phenylacrylate (3q)

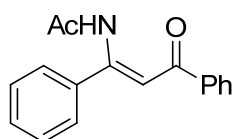


3q was obtained as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 10.64 (s, 1H), 7.49 – 7.29 (m, 5H), 5.28 (s, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 2.16 (s, 3H), 1.32 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 168.70, 168.52, 154.59, 136.00, 129.65, 128.13, 127.15, 101.18, 60.39, 24.88, 14.36 ppm.

HRMS (ESI): m/z calculated for $\text{C}_{13}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{Na}]^+$: 256.0950, found: 256.0948.

FTIR: 3293, 2979, 1723, 1672, 1622, 1491, 1285, 1179, 1036, 769, 697 cm^{-1}

(Z)-N-(3-oxo-1,3-diphenylprop-1-en-1-yl)acetamide (3r)

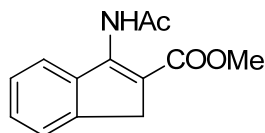


3r was obtained as yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 12.27 (s, 1H), 8.00 – 7.93 (m, 2H), 7.61 – 7.53 (m, 1H), 7.52 – 7.38 (m, 7H), 6.33 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 191.79, 169.03, 156.36, 138.71, 136.33, 132.87, 129.93, 128.78, 128.21, 127.93, 127.50, 104.90, 25.21 ppm.

HRMS (ESI): m/z calculated for $\text{C}_{17}\text{H}_{15}\text{NO}_2$ $[\text{M}+\text{Na}]^+$: 288.1000, found: 288.0009.

FTIR: 3294, 3059, 1718, 1623, 1570, 1442, 1289, 1211, 1043, 759, 694, 525 cm^{-1}

methyl 3-acetamido-1H-indene-2-carboxylate (4a)

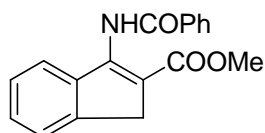


4a was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.18 (s, 1H), 8.15 – 8.17 (m, 1H), 7.52 – 7.32 (m, 3H), 3.85 (s, 3H), 3.62 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 168.56, 167.74, 151.38, 143.75, 137.96, 128.79, 126.94, 126.72, 124.10, 112.89, 51.57, 35.51, 24.75 ppm.

HRMS (ESI): m/z calculated for $\text{C}_{13}\text{H}_{13}\text{NO}_3$ $[\text{M}+\text{Na}]^+$: 254.0793, found: 254.0795.

FTIR: 3288, 2953, 1703, 1674, 1618, 1501, 1379, 1329, 1198, 762, 636, 528 cm^{-1}

methyl 3-benzamido-1H-indene-2-carboxylate (**4b**)

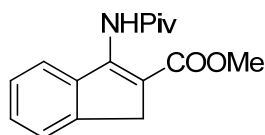


4b was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 11.20 (s, 1H), 8.48 – 8.25 (m, 1H), 8.22 – 8.01 (m, 2H), 7.65 – 7.34 (m, 6H), 3.86 (s, 3H), 3.67 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ = 168.15, 165.13, 151.98, 143.92, 137.87, 133.86, 132.62, 129.03, 128.89, 128.07, 127.23, 126.80, 124.17, 113.29, 51.71, 35.61 ppm.

HRMS (ESI): m/z calculated for $\text{C}_{18}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{Na}]^+$: 316.0950, found: 316.0948.

FTIR: 3274, 2947, 1692, 1662, 1613, 1565, 1328, 1271, 1204, 1010, 757, 705, 762 cm^{-1}

methyl 3-pivalamido-1H-indene-2-carboxylate (**4c**)

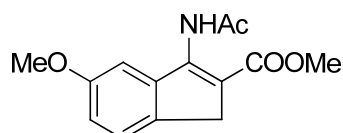


4c was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.51 (s, 1H), 8.22 – 8.13 (m, 1H), 7.52 – 7.28 (m, 3H), 3.85 (s, 3H), 3.61 (s, 2H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ = 177.42, 167.86, 151.99, 143.87, 138.06, 128.72, 127.11, 126.65, 124.06, 112.83, 51.59, 40.18, 35.54, 27.77 ppm.

HRMS (ESI): m/z calculated for $\text{C}_{16}\text{H}_{19}\text{NO}_3$ $[\text{M}+\text{Na}]^+$: 296.1263, found: 296.1254.

FTIR: 3306, 2965, 1702, 1677, 1617, 1491, 1255, 1204, 759, 554 cm^{-1}

methyl 3-acetamido-5-methoxy-1H-indene-2-carboxylate (4d)

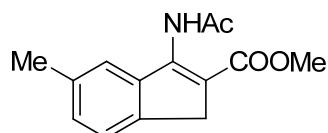


4d was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.25 (s, 1H), 7.80 (d, $J = 2.6$ Hz, 1H), 7.31 (d, $J = 8.3$ Hz, 1H), 6.97 (d, $J = 8.2$ Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.53 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 168.60, 167.75, 158.75, 151.41, 139.03, 136.19, 124.56, 116.97, 113.85, 110.75, 55.66, 51.56, 34.75, 24.80$ ppm.

HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{15}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 284.0899, found: 284.0896

FTIR: 3286, 2957, 1717, 1668, 1594, 1570, 1303, 1258, 1230, 1030, 819, 764, 554 cm^{-1}

methyl 3-acetamido-5-methyl-1H-indene-2-carboxylate(4e)

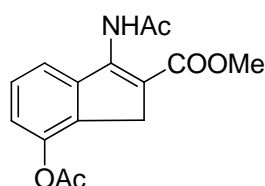


4e was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.14 (s, 1H), 7.95 (s, 1H), 7.32 (d, $J = 7.7$ Hz, 1H), 7.19 (d, $J = 7.7$ Hz, 1H), 3.83 (s, 3H), 3.55 (s, 2H), 2.41 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 168.59, 167.76, 151.36, 140.97, 138.13, 136.38, 129.90, 127.15, 123.78, 113.29, 51.52, 35.11, 24.74, 21.74$ ppm.

HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{Na}]^+$: 268.0950, found: 268.0946.

FTIR: 3278, 2946, 1688, 1593, 1432, 1304, 1253, 1193, 1084, 813, 682 cm^{-1}

methyl 3-acetamido-7-acetoxy-1H-indene-2-carboxylate (4f)

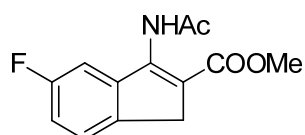


4f was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.13 (s, 1H), 8.07 (d, $J = 7.7$ Hz, 1H), 7.37 (t, $J = 8.0$ Hz, 1H), 7.12 (d, $J = 8.0$ Hz, 1H), 3.84 (s, 3H), 3.51 (s, 2H), 2.35 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 168.80, 168.55, 167.44, 150.80, 146.43, 140.11, 135.20, 128.22, 125.09, 121.99, 113.04, 51.66, 32.87, 24.73, 21.02$ ppm.

HRMS (ESI): m/z calculated for $\text{C}_{15}\text{H}_{15}\text{NO}_5$ $[\text{M}+\text{Na}]^+$: 312.0848, found: 312.0845.

FTIR: 3288, 2954, 1766, 1701, 1673, 1504, 1385, 1210, 953, 750, 672, 551 cm^{-1}

methyl 3-acetamido-5-fluoro-1H-indene-2-carboxylate(**4g**)

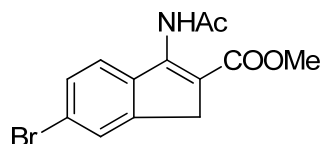


4g was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.17 (s, 1H), 7.92 (dd, $J = 10.1, 2.5$ Hz, 1H), 7.34 (dd, $J = 8.3, 5.1$ Hz, 1H), 7.07 (td, $J = 8.6, 2.5$ Hz, 1H), 3.84 (s, 3H), 3.55 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) $\delta = 168.58, 167.47, 161.85$ ($J = 241$), 150.58 ($J = 3$), 139.55 ($J = 10$), 139.06 ($J = 2$), 124.85 ($J = 8$), 116.05 ($J = 23$), $114.55, 114.03$ ($J = 25$), $51.68, 34.88, 24.68$ ppm.

HRMS (ESI): m/z calculated for $\text{C}_{13}\text{H}_{12}\text{FNO}_3$ $[\text{M}+\text{Na}]^+$: 272.0699, found: 272.0696

FTIR: 3219, 2955, 1713, 1663, 1575, 1431, 1298, 1207, 823, 771, 549 cm^{-1}

methyl 3-acetamido-6-bromo-1H-indene-2-carboxylate (**4h**)

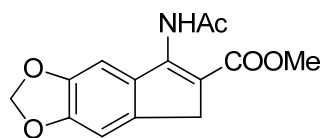


4h was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.20 (s, 1H), 8.06 (d, $J = 8.5$ Hz, 1H), 7.58 (s, 1H), 7.48 (d, $J = 8.6$, 1H), 3.85 (s, 3H), 3.59 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 168.62, 167.50, 150.64, 145.57, 136.89, 130.01, 128.40, 127.34, 123.53, 112.82, 51.70, 35.38, 24.75$ ppm.

HRMS (ESI): m/z calculated for $\text{C}_{13}\text{H}_{12}\text{BrNO}_3$ $[\text{M}+\text{Na}]^+$: 331.9898, found: 331.9895.

FTIR: 3284, 2958, 1685, 1681, 1613, 1326, 1247, 1201, 854, 649 cm^{-1}

methyl 7-acetamido-5H-indeno[5,6-d][1,3]dioxole-6-carboxylate (**4i**)

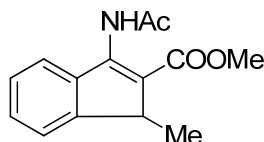


4i was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.20 (s, 1H), 7.67 (s, 1H), 6.89 (s, 1H), 6.00 (s, 2H), 3.82 (s, 3H), 3.52 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 168.63, 167.41, 151.54, 149.37, 147.01, 139.63, 131.60, 111.71, 107.13, 104.65, 101.64, 51.41, 35.34, 24.76 ppm.

HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{13}\text{NO}_5$ $[\text{M}+\text{Na}]^+$: 298.0691, found: 298.0695

FTIR: 3289, 2950, 1688, 1671, 1587, 1469, 1385, 1231, 1035, 933, 669 cm^{-1}

methyl 3-acetamido-1-methyl-1H-indene-2-carboxylate (**4j**)

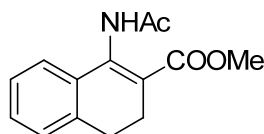


4j was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.26 (s, 1H), 8.19 – 8.04 (m, 1H), 7.46 – 7.29 (m, 3H), 3.86 (s, 3H), 3.69 (q, J = 7.3 Hz, 1H), 2.29 (s, 3H), 1.41 (d, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 168.62, 167.86, 151.03, 150.18, 136.38, 129.06, 126.99, 126.79, 123.00, 118.34, 51.47, 41.47, 24.78, 17.33 ppm.

HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{Na}]^+$: 268.0950, found: 268.0947

FTIR: 3302, 2950, 1715, 1664, 1614, 1568, 1385, 1254, 1196, 1091, 756, 536 cm^{-1}

methyl 1-acetamido-3,4-dihydronaphthalene-2-carboxylate (**4k**)



4k was obtained as white solid. ^1H NMR (400 MHz, CDCl_3) δ 10.14 (s, 1H), 7.33 (dd, J = 7.6, 1.5 Hz, 1H), 7.27 – 7.13 (m, 3H), 3.80 (s, 3H), 2.77 (t, J = 7.6 Hz, 2H), 2.57 (t, J = 7.6 Hz, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ = 169.64, 169.12,

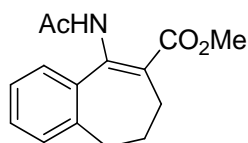
145.71, 137.87, 130.22, 129.73, 127.41, 127.01, 126.00, 113.71, 52.02, 27.72, 24.65, 22.38 ppm.

HRMS (ESI): m/z calculated for C₁₄H₁₅NO₃ [M+Na]⁺: 268.0950, found: 268.0942

FTIR: 3259, 2945, 2835, 1696, 1664, 1527, 1313, 1122, 997, 766, 729, 575 cm⁻¹

methyl 9-acetamido-6,7-dihydro-5H-benzo[7]annulene-8-carboxylate

(4I)



4I was obtained as white solid. ¹H NMR (400 MHz, CDCl₃) δ 10.61 (s, 1H), 7.31 – 7.19 (m, 4H), 3.80 (s, 3H), 2.66 (t, *J* = 6.6 Hz, 2H), 2.21 – 1.98 (m, 7H). ¹³C NMR (100 MHz, CDCl₃) δ = 169.94, 168.76, 148.81, 140.53, 135.96, 129.18, 128.85, 127.45, 125.83, 110.51, 51.90, 34.65, 31.42, 24.77, 23.92 ppm.

HRMS (ESI): m/z calculated for C₁₅H₁₇NO₃ [M+Na]⁺: 282.1106, found: 282.1102

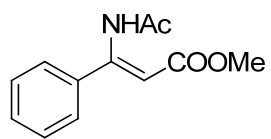
FTIR: 3252, 3016, 2935, 1708, 1669, 1620, 1530, 1427, 1324, 1199, 767, 561cm⁻¹

4. References

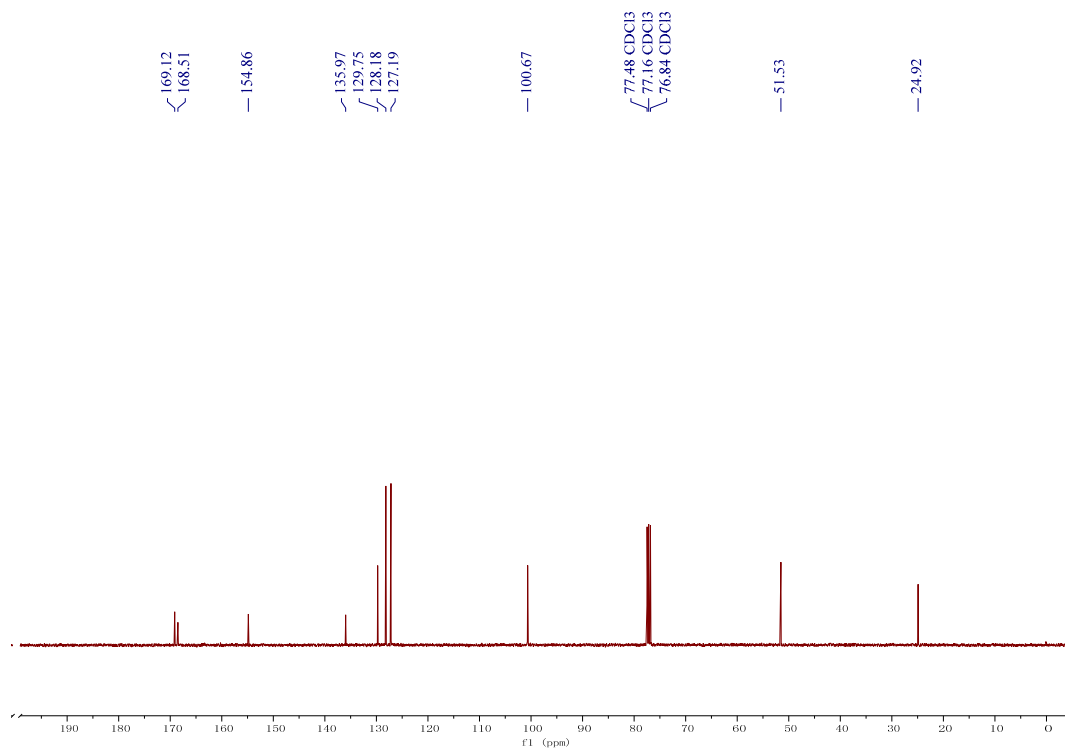
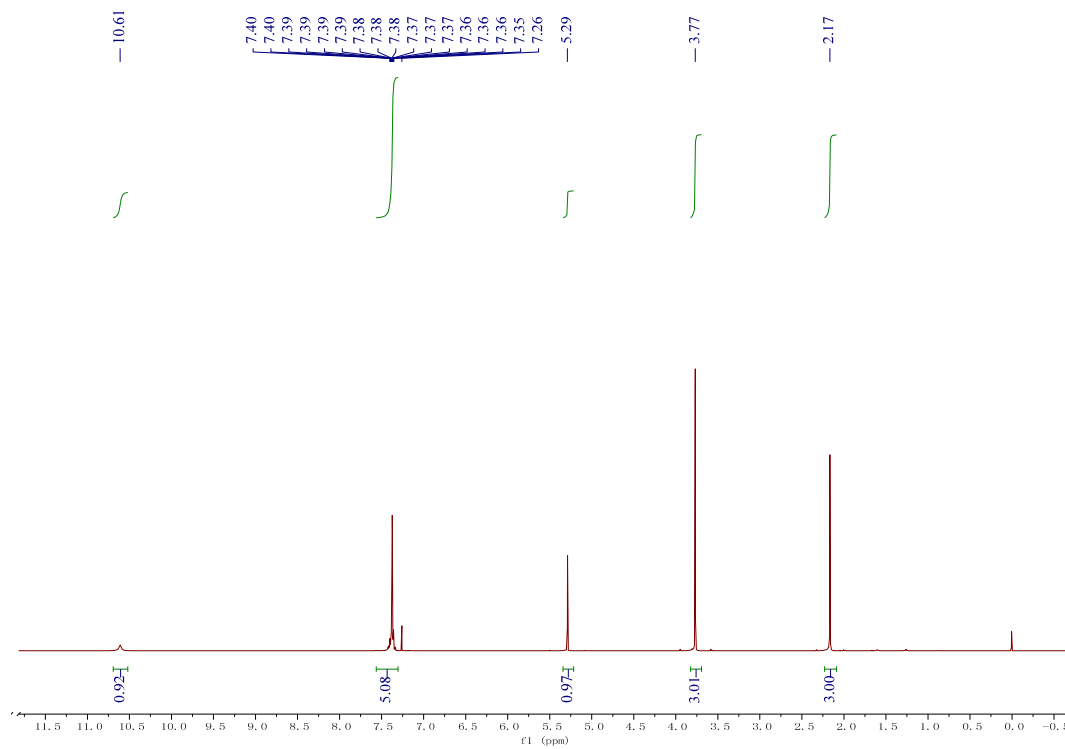
[1] Taniguchi, T.; Sugiura, Y.; Zaimoku, H.; Ishibashi, H. *Angew.Chem., Int. Ed.* 2010, 49, 10154.

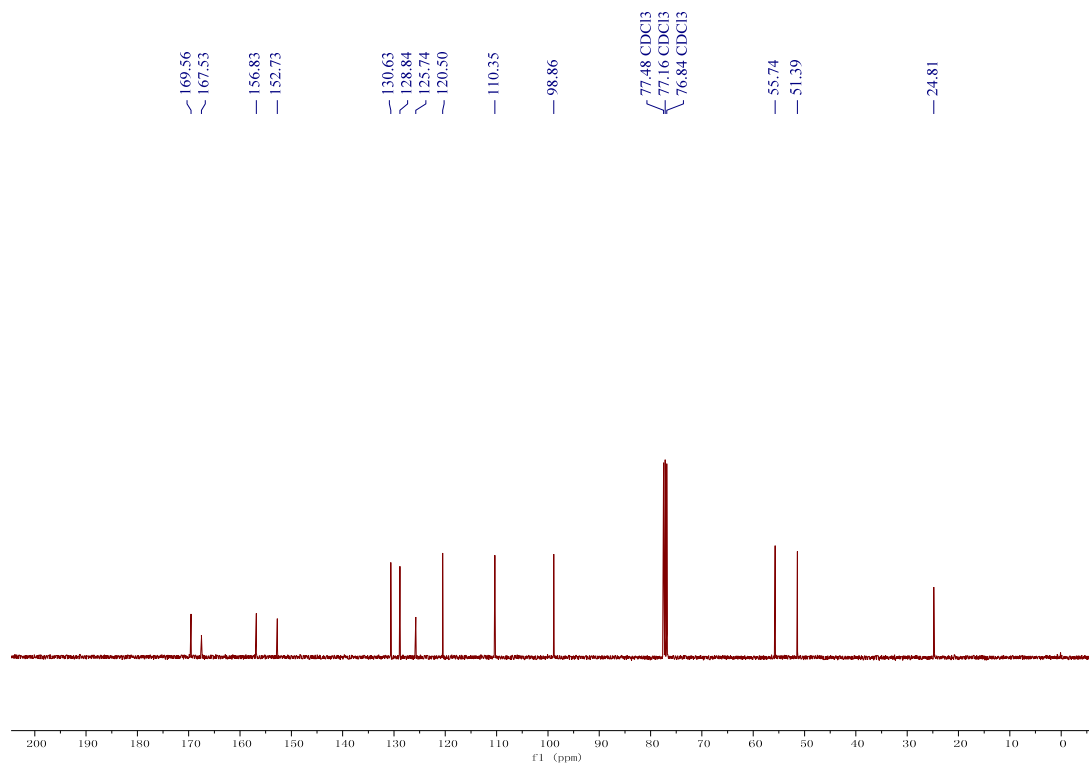
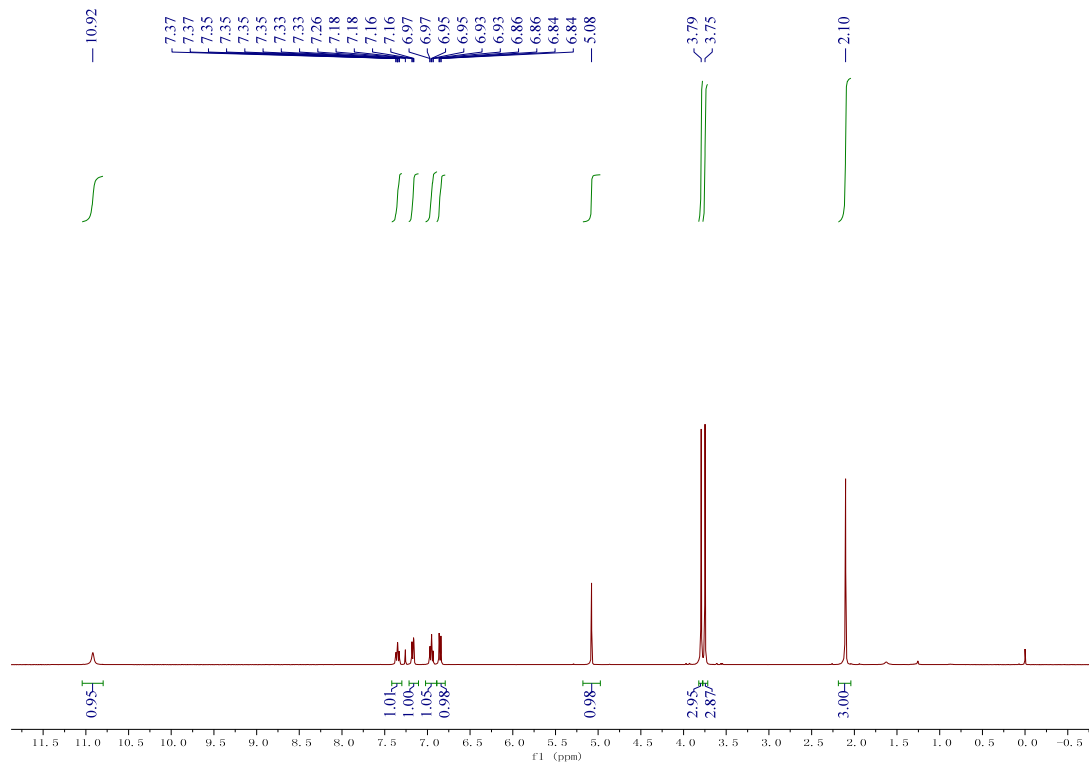
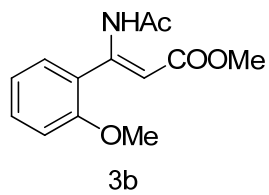
[2] Ch Chen.; E Zhan.; Y Li.;W Shen. *J. Mole .Cat A:Chemical.*2013, 379,117.

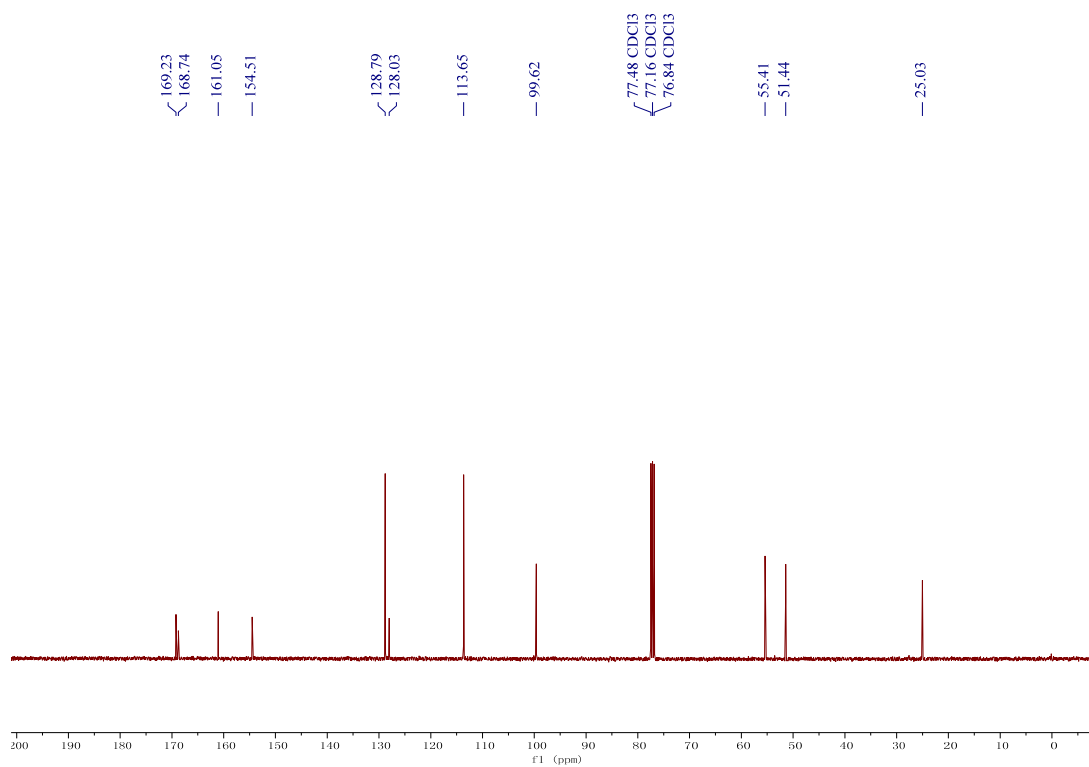
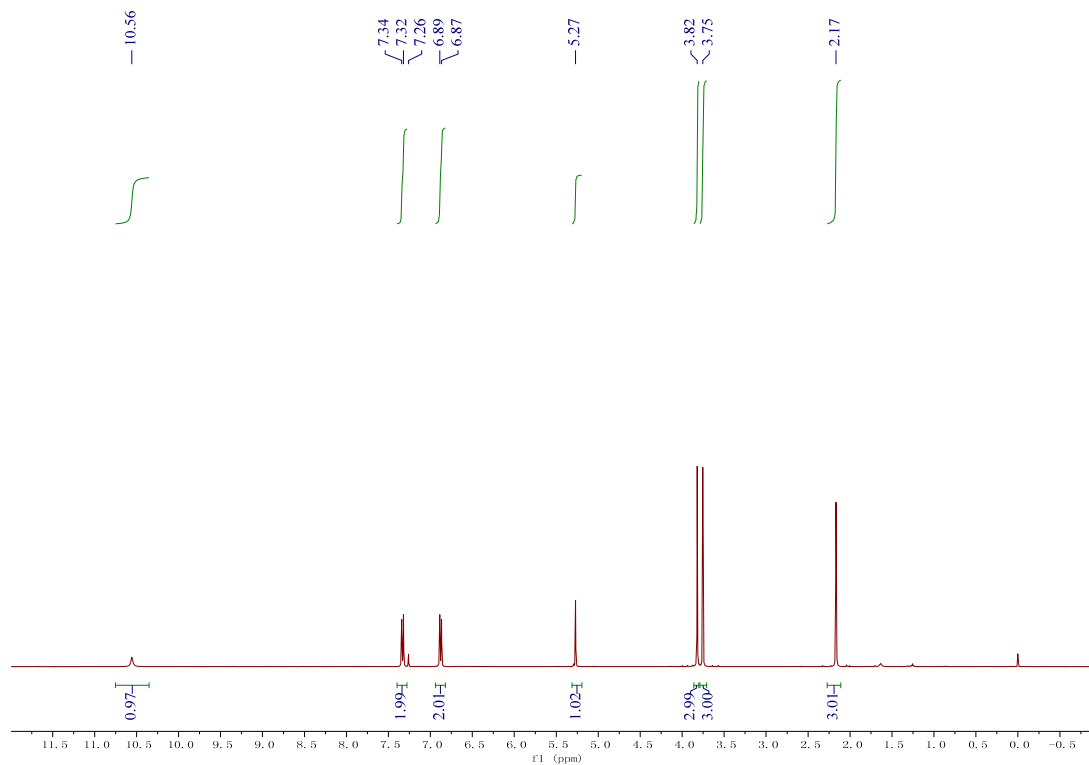
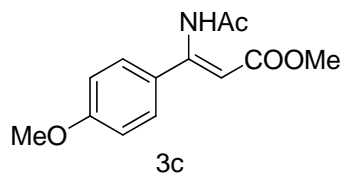
6. NMR spectra for the products

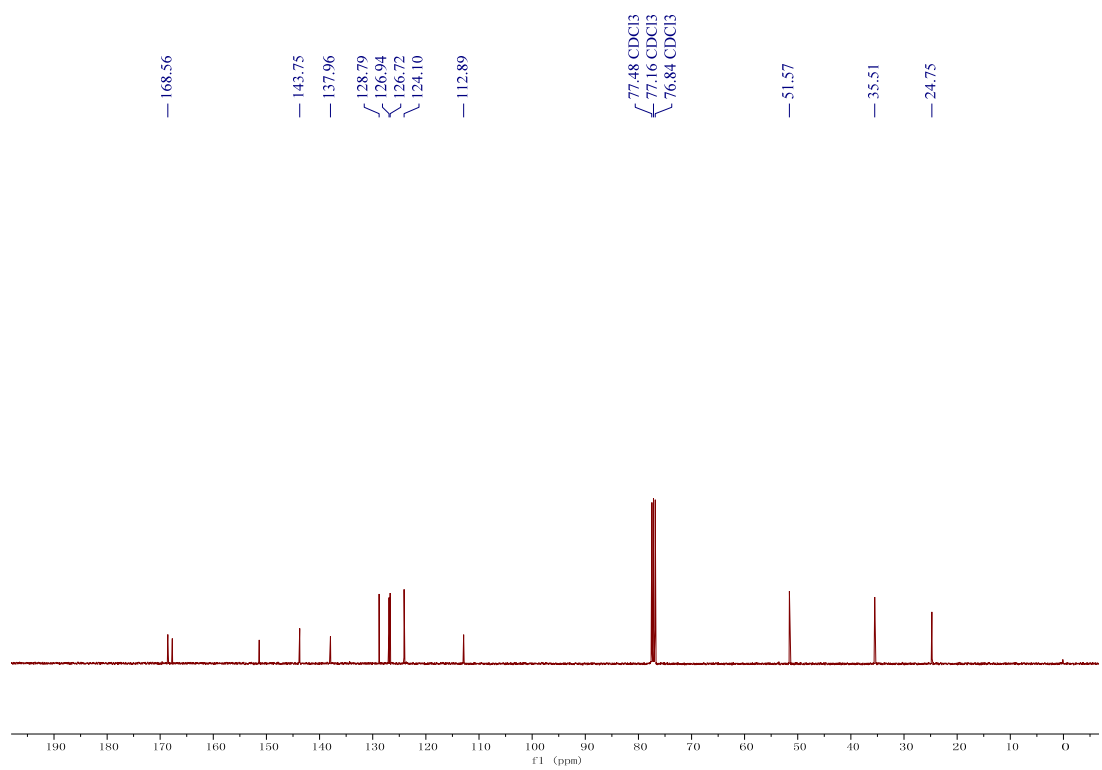
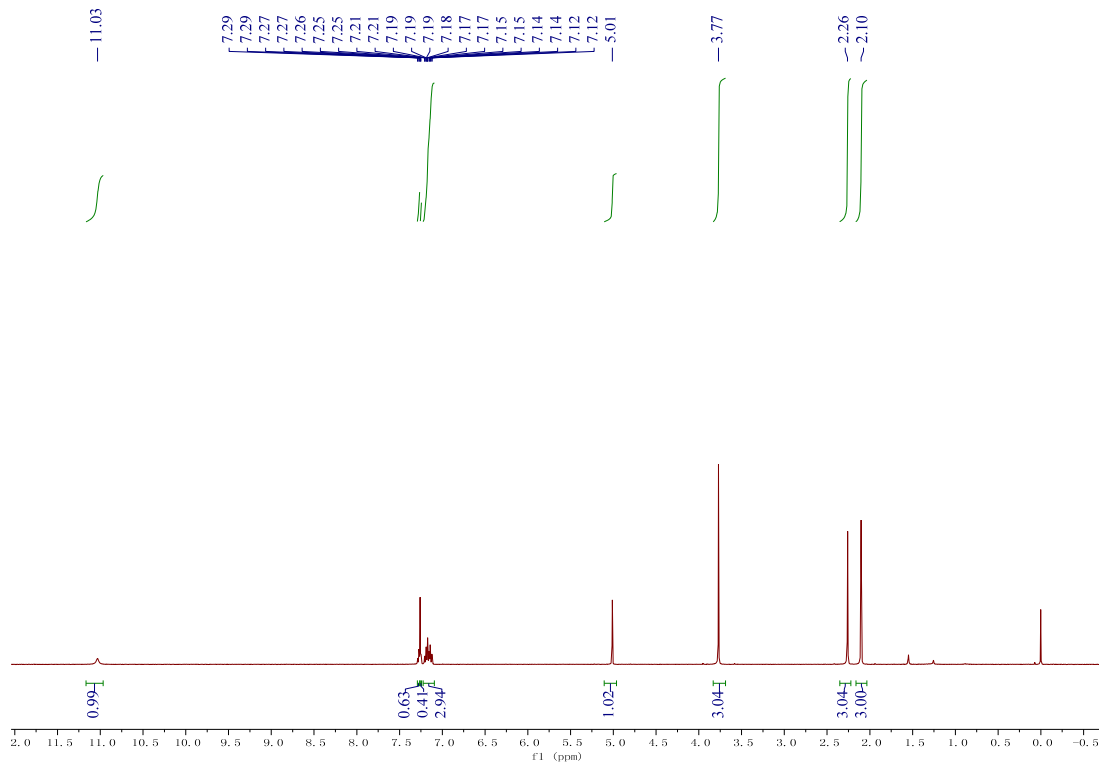
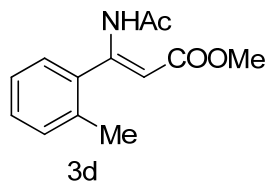


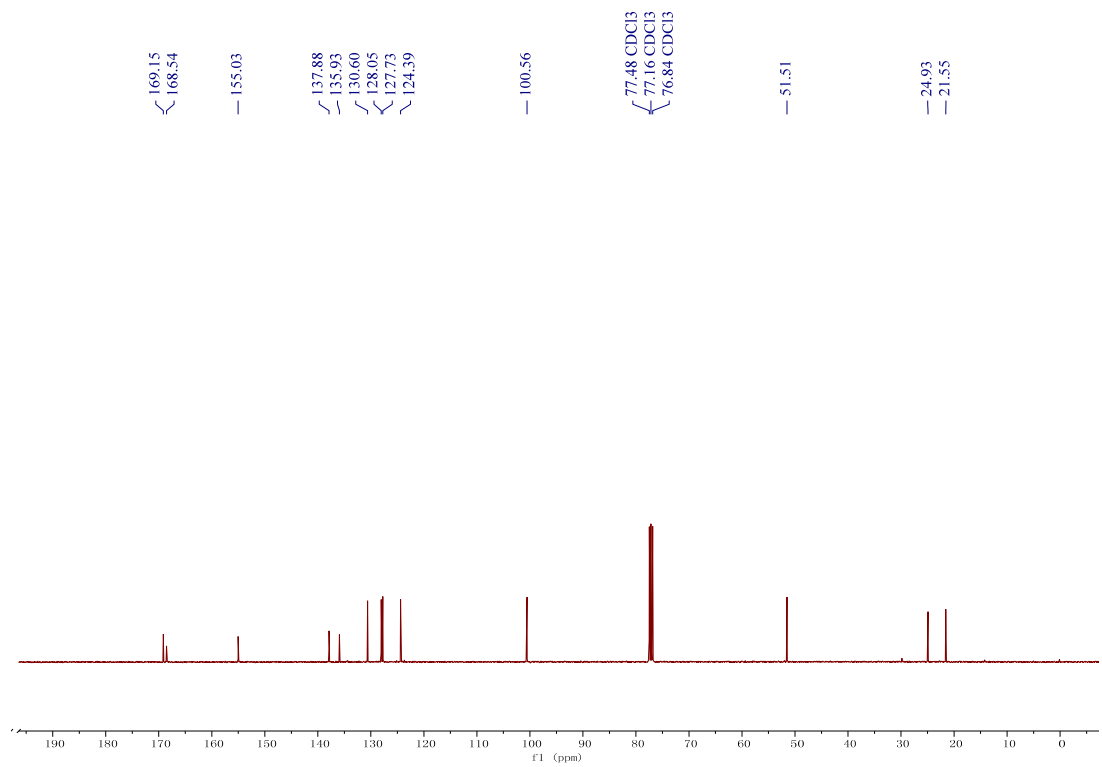
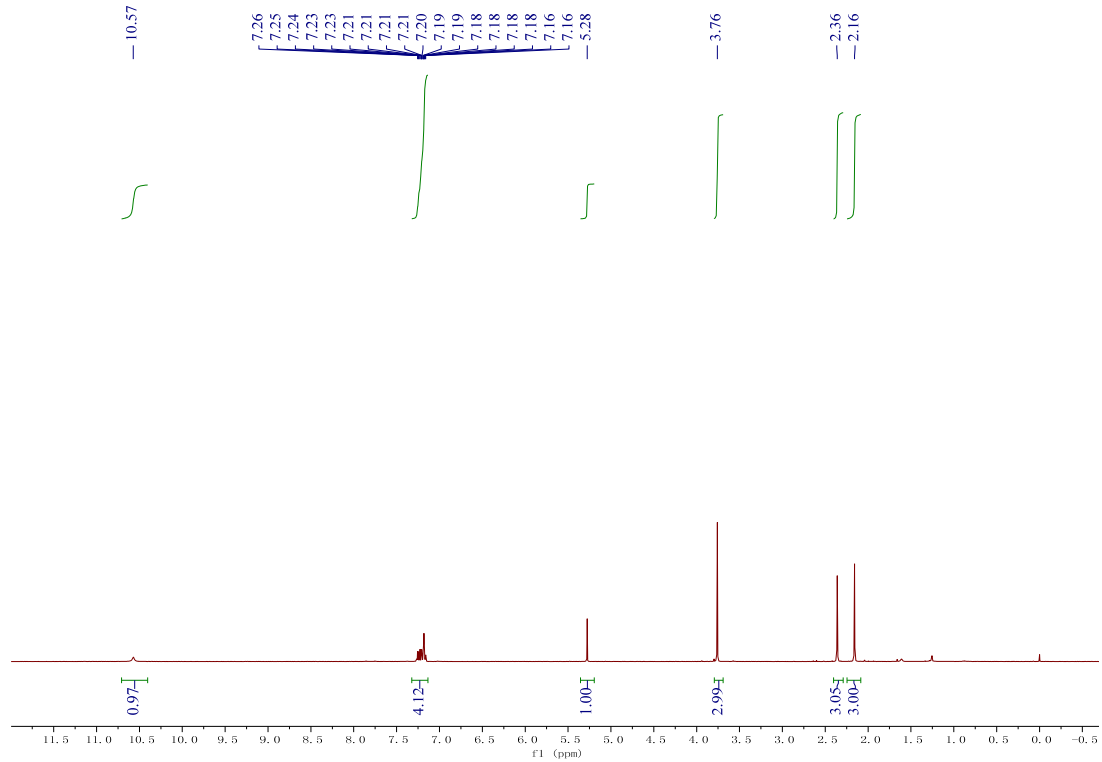
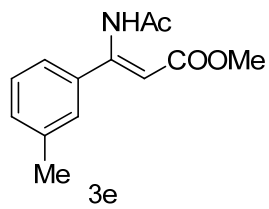
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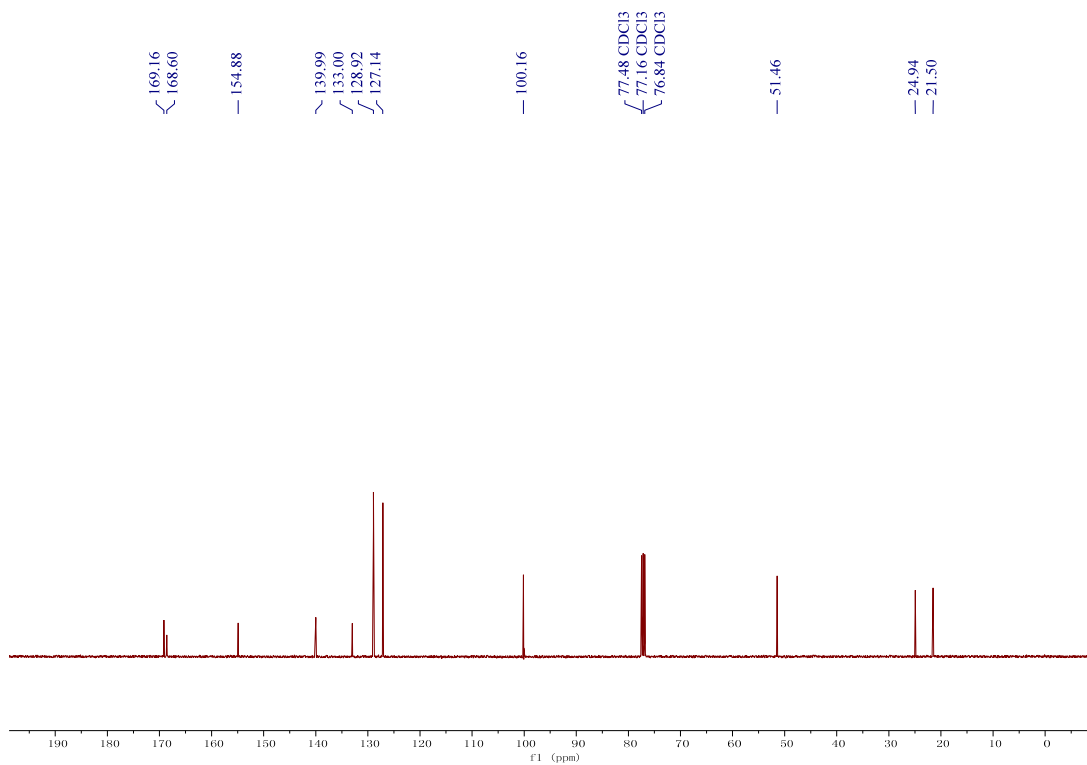
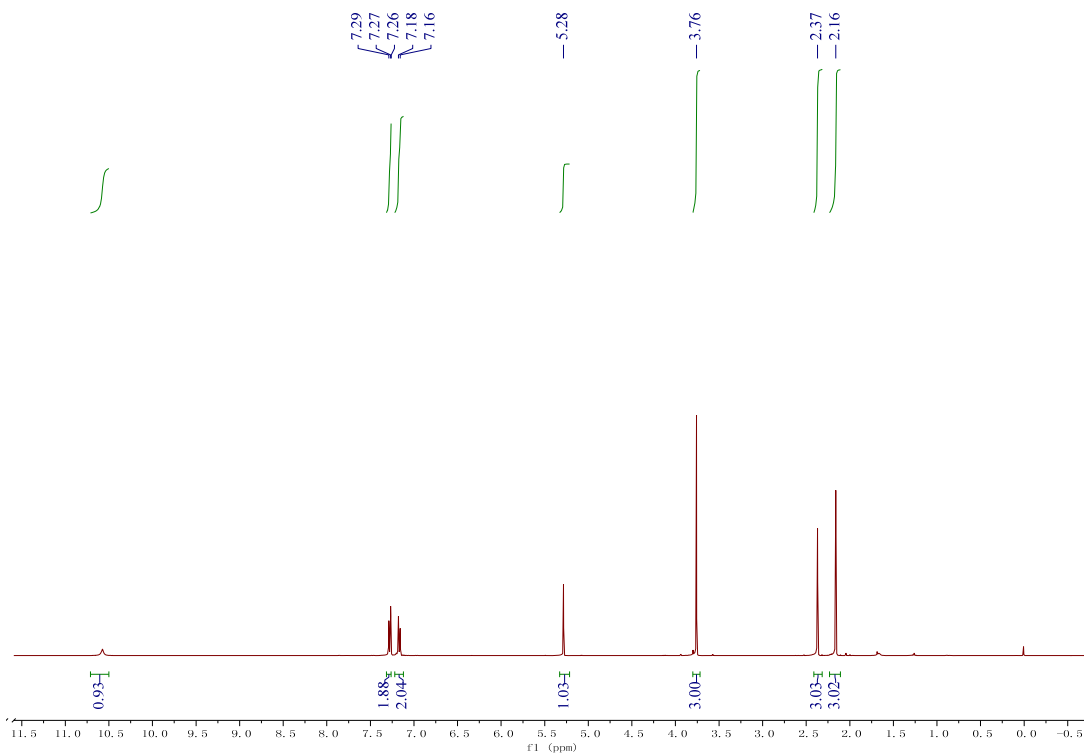
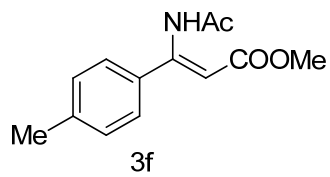


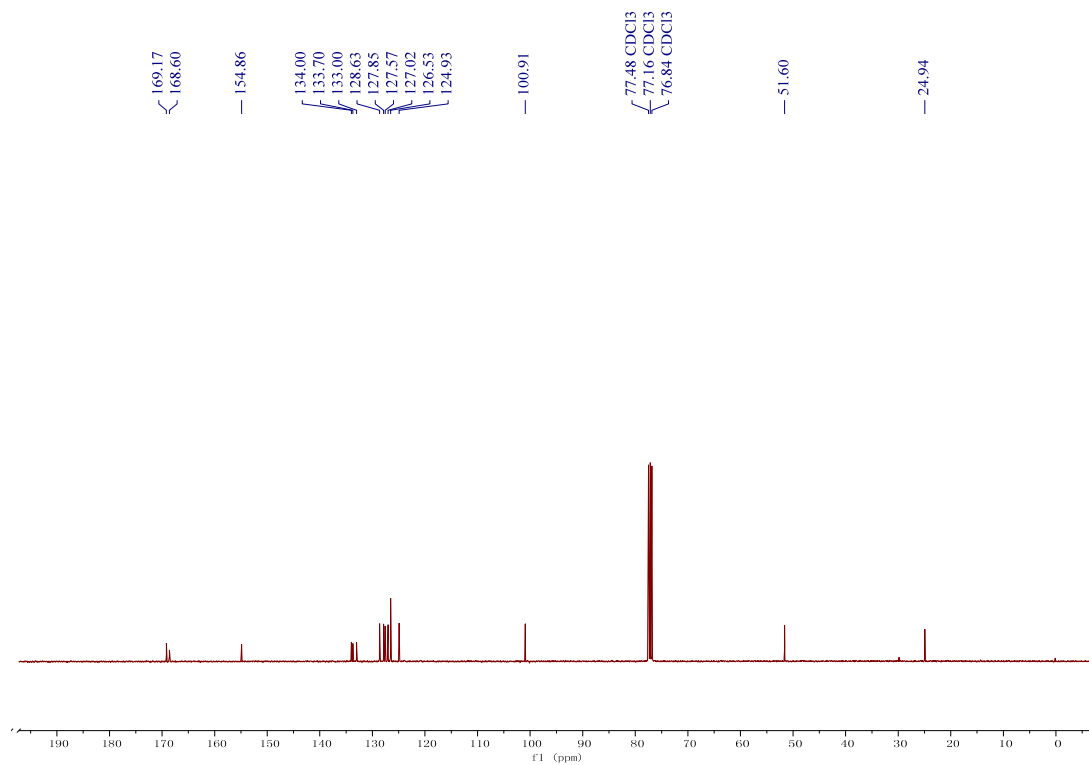
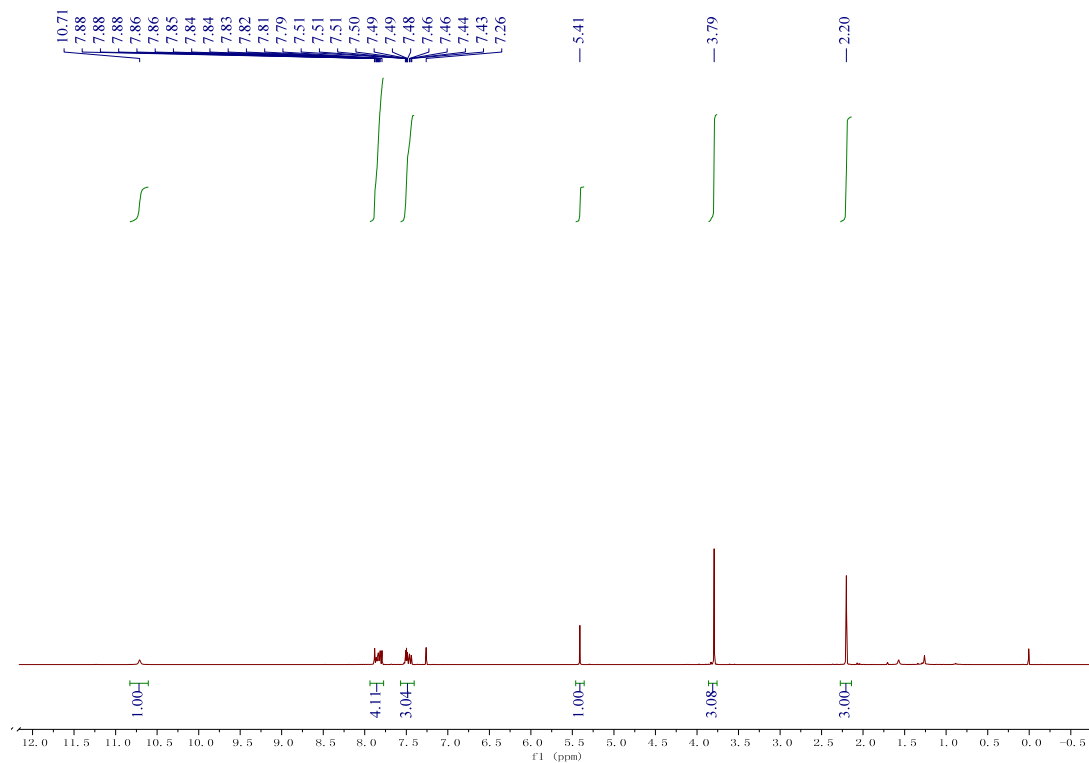
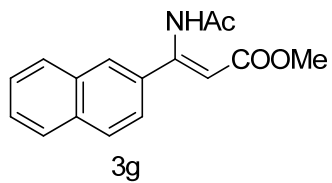


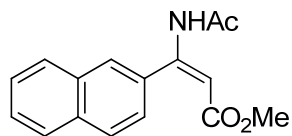




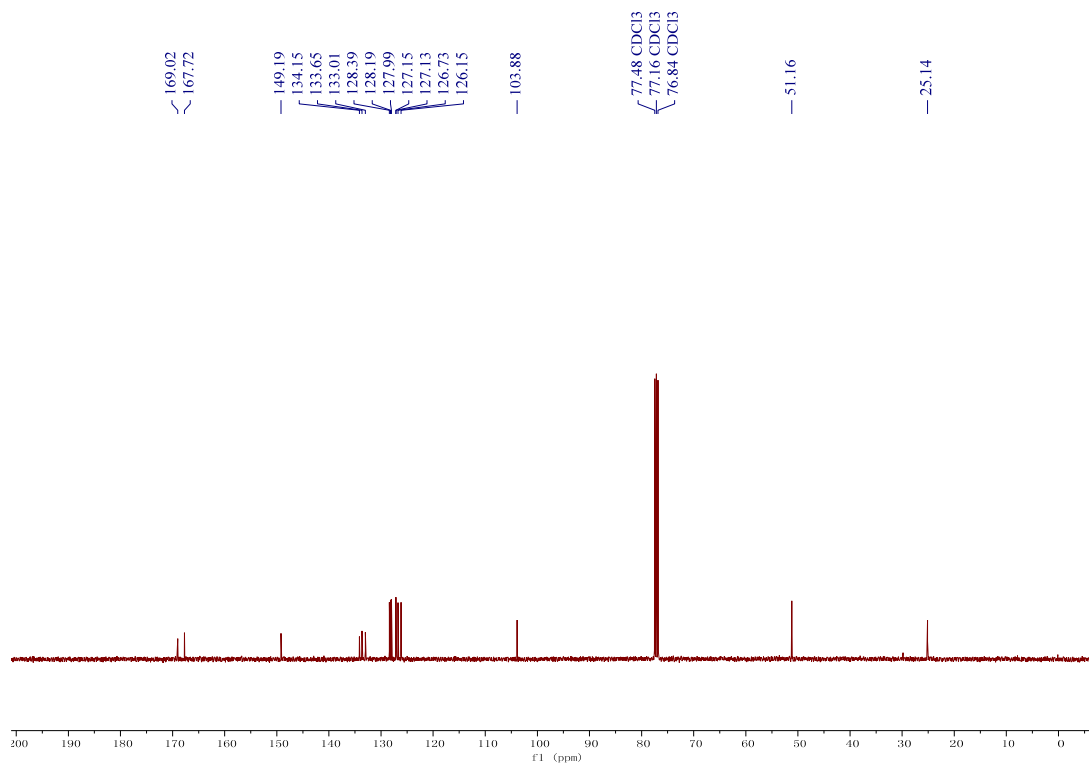
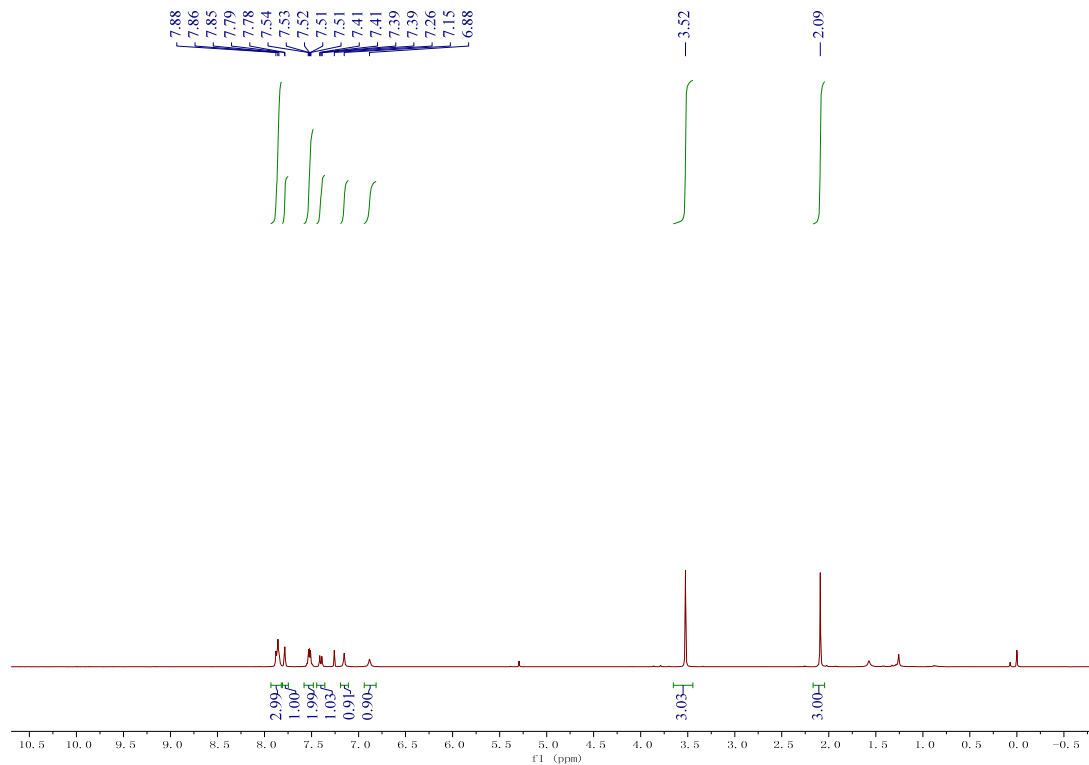


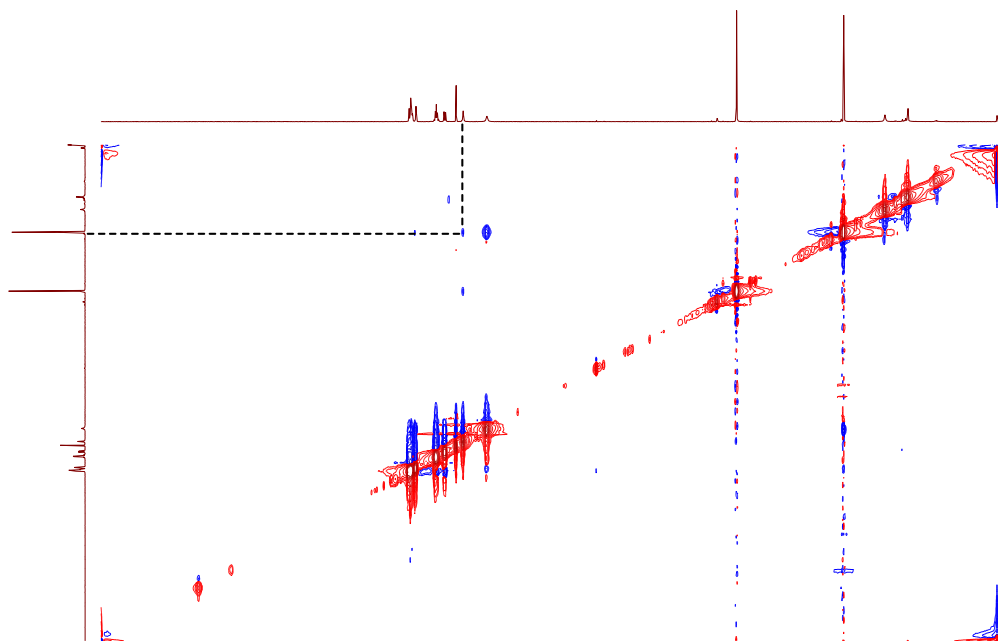
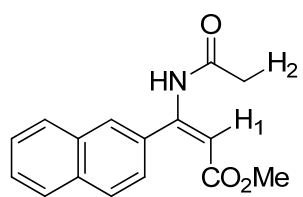


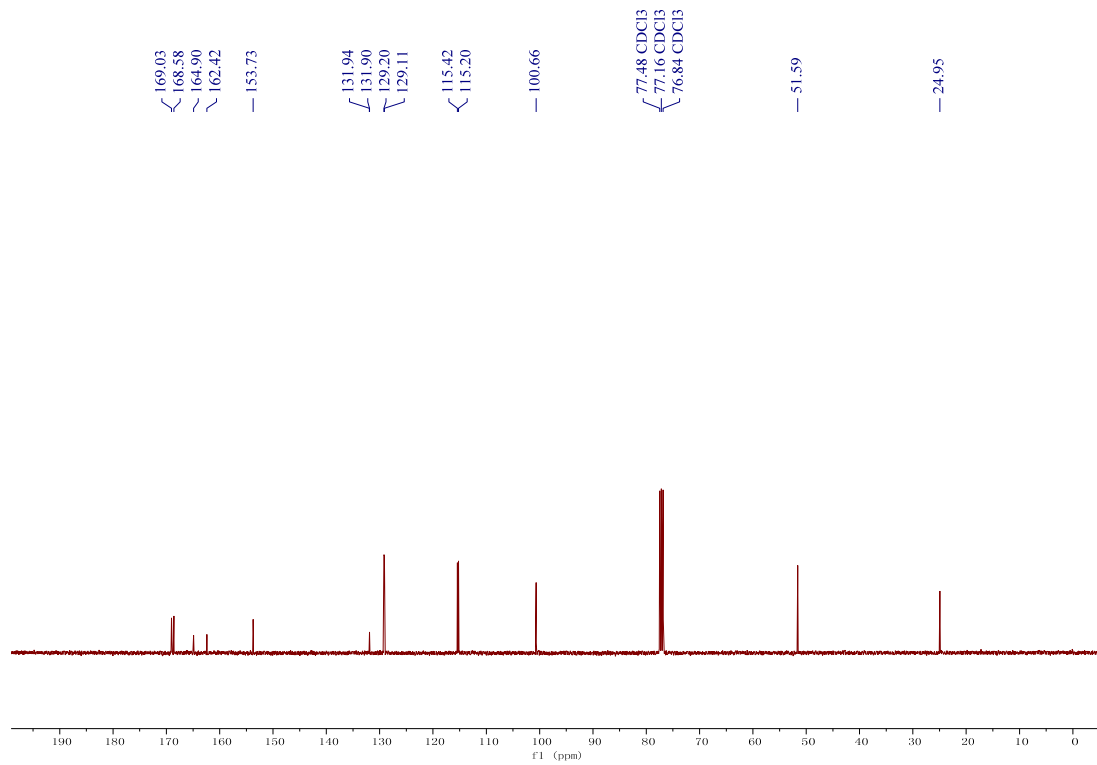
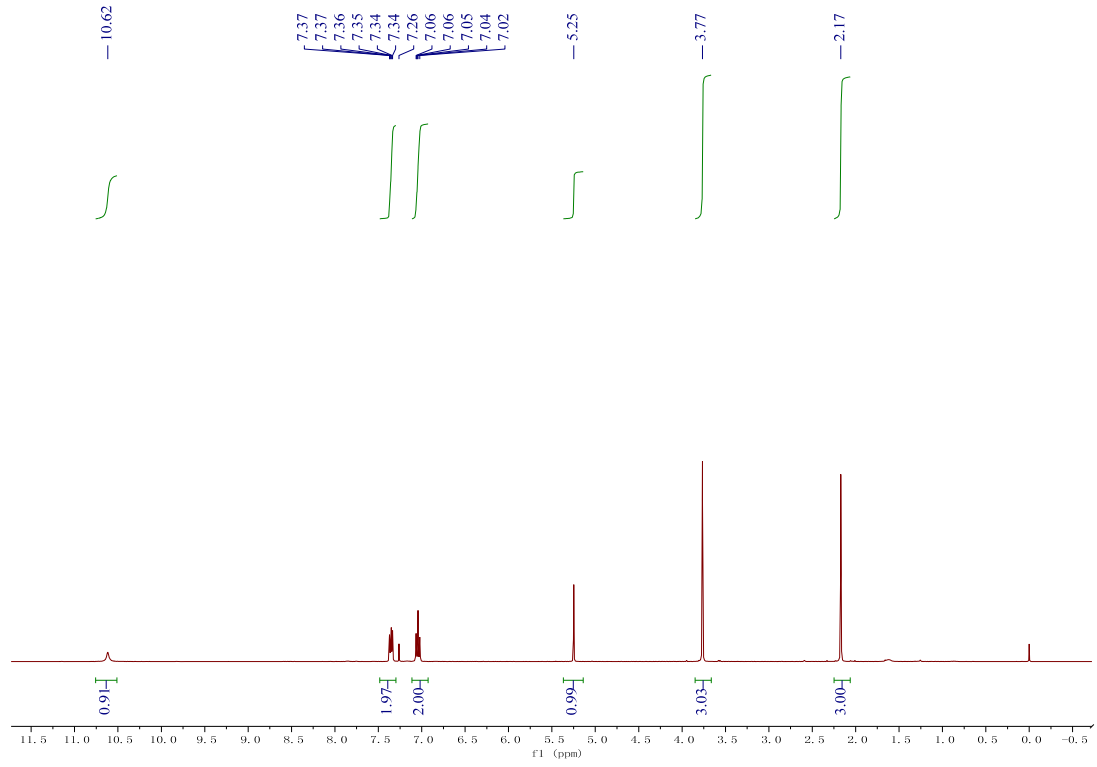
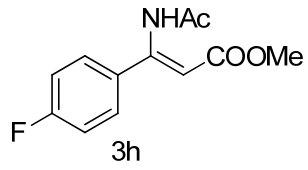


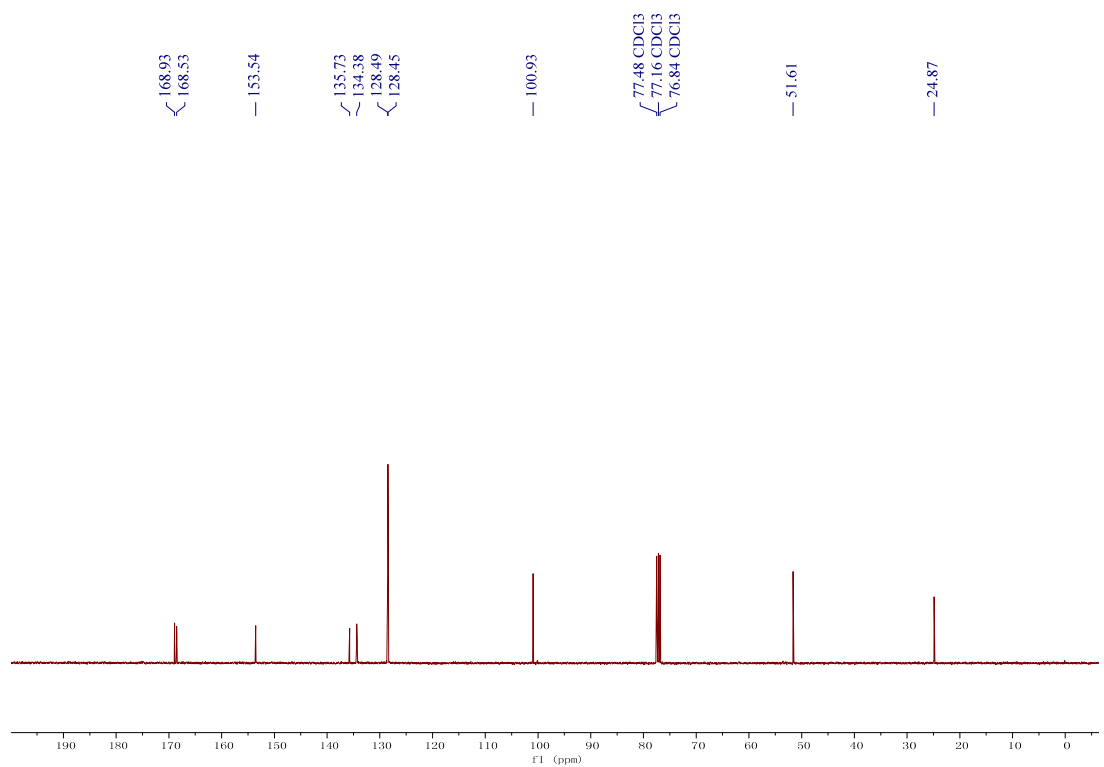
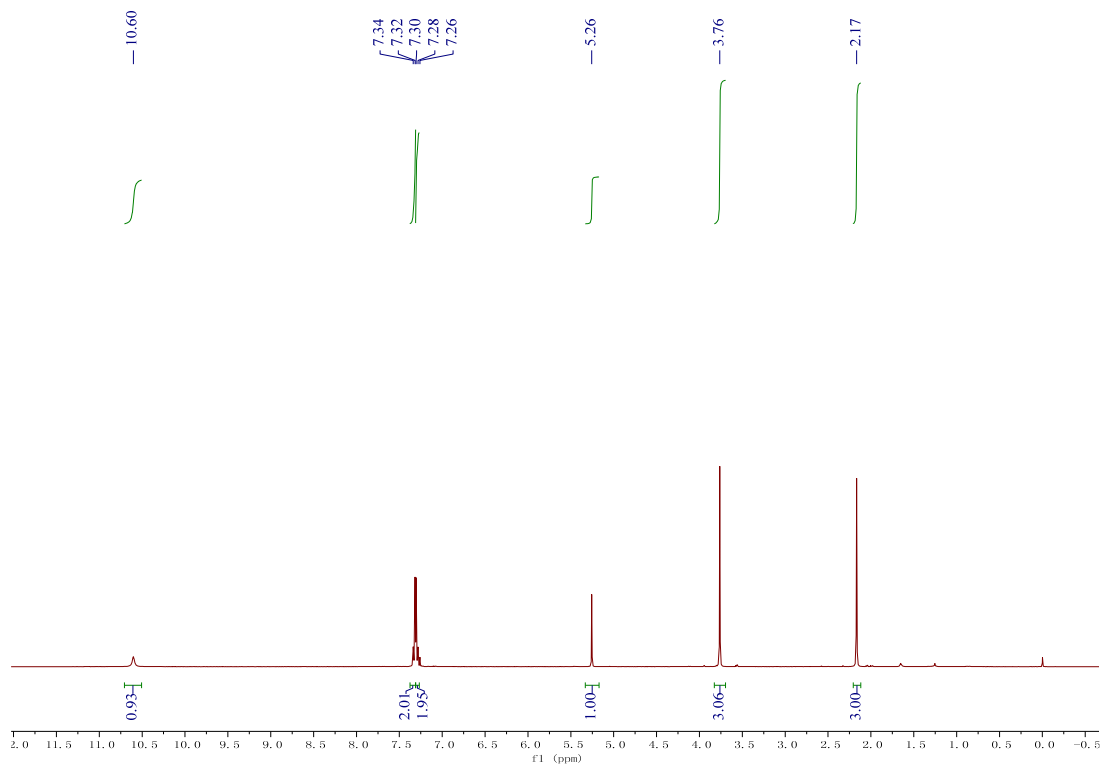
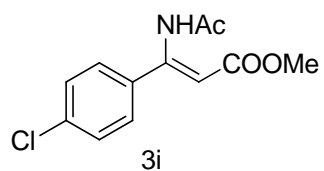


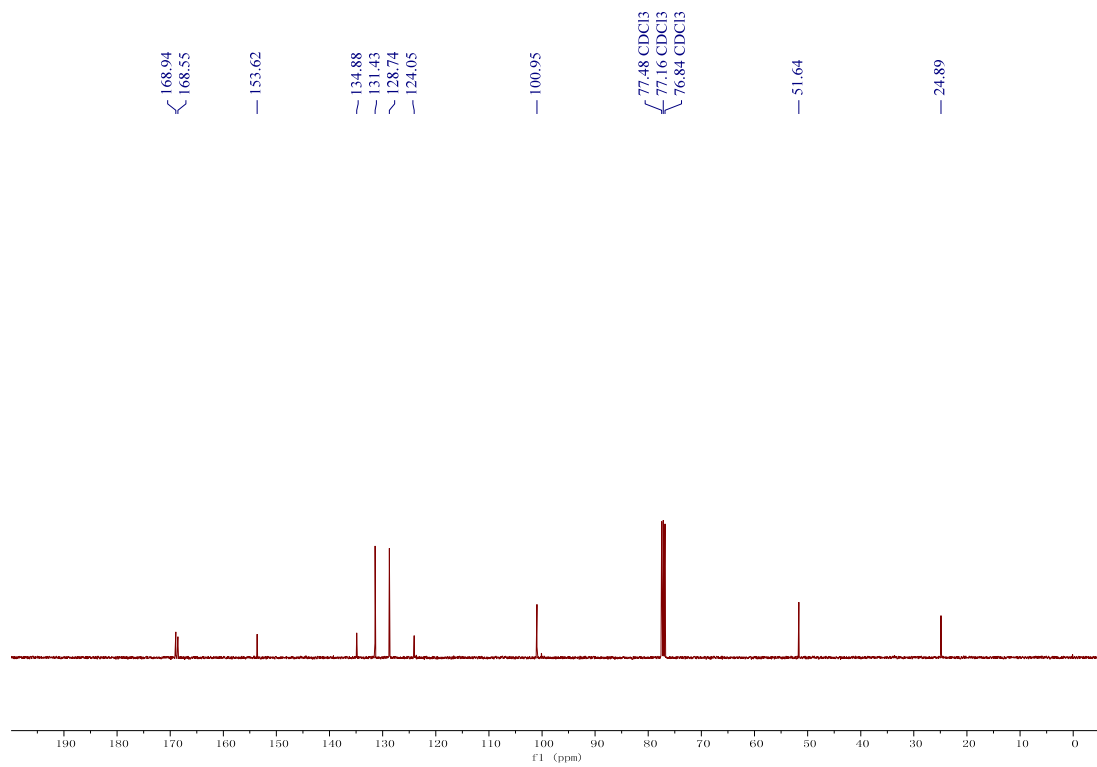
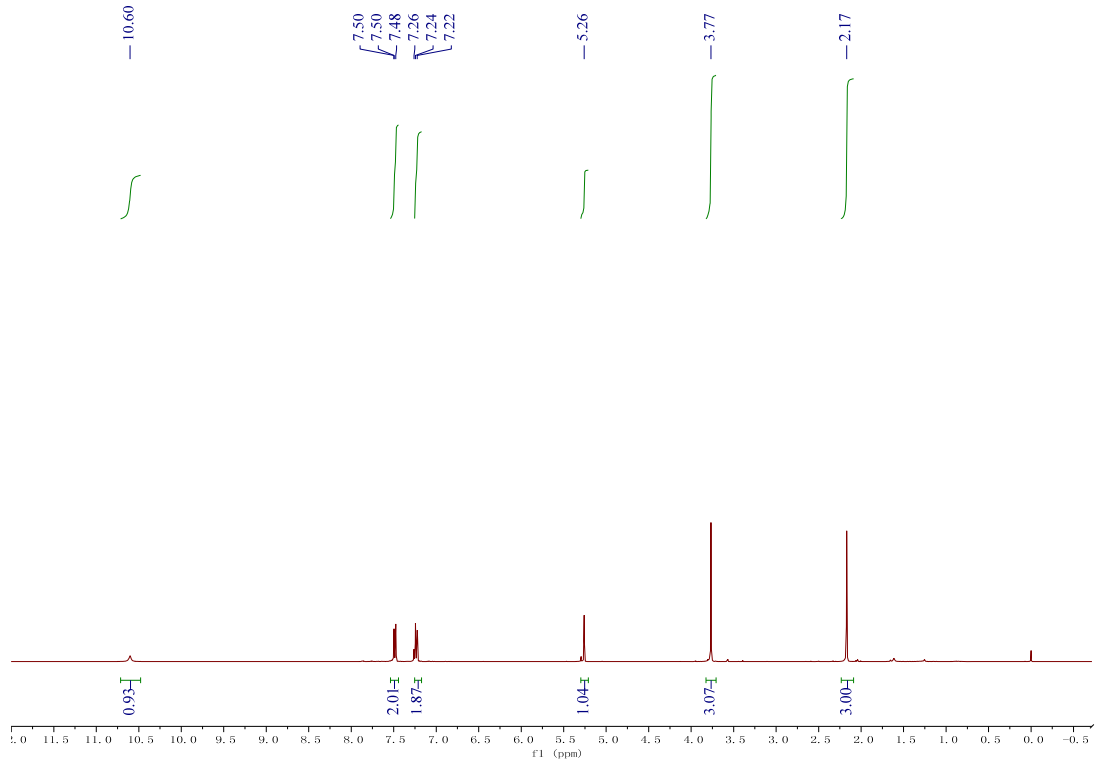
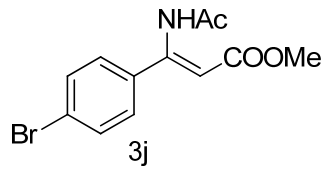
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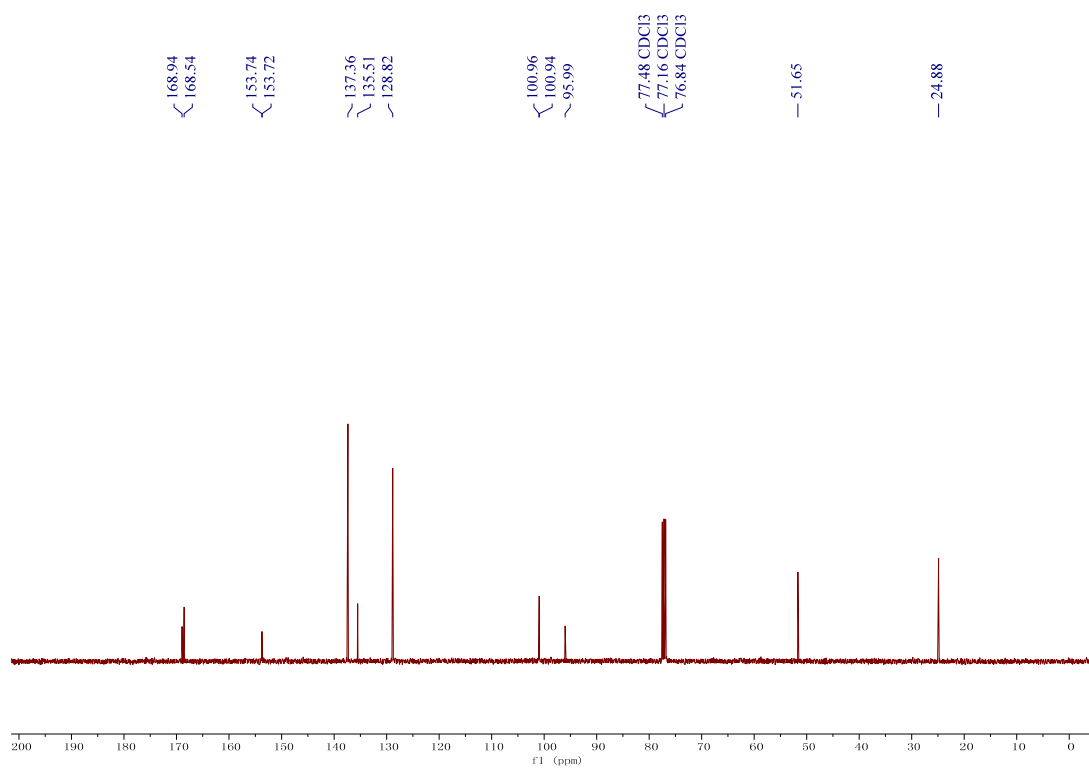
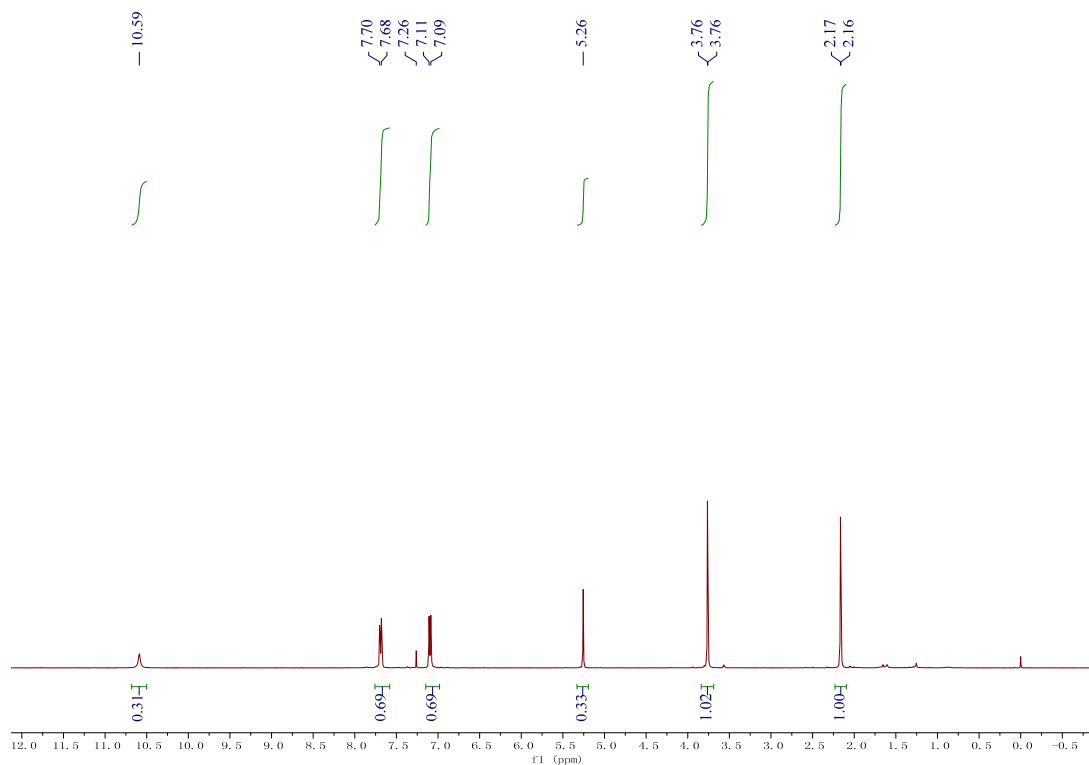
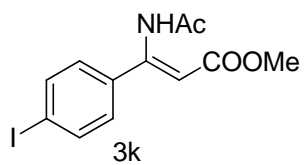


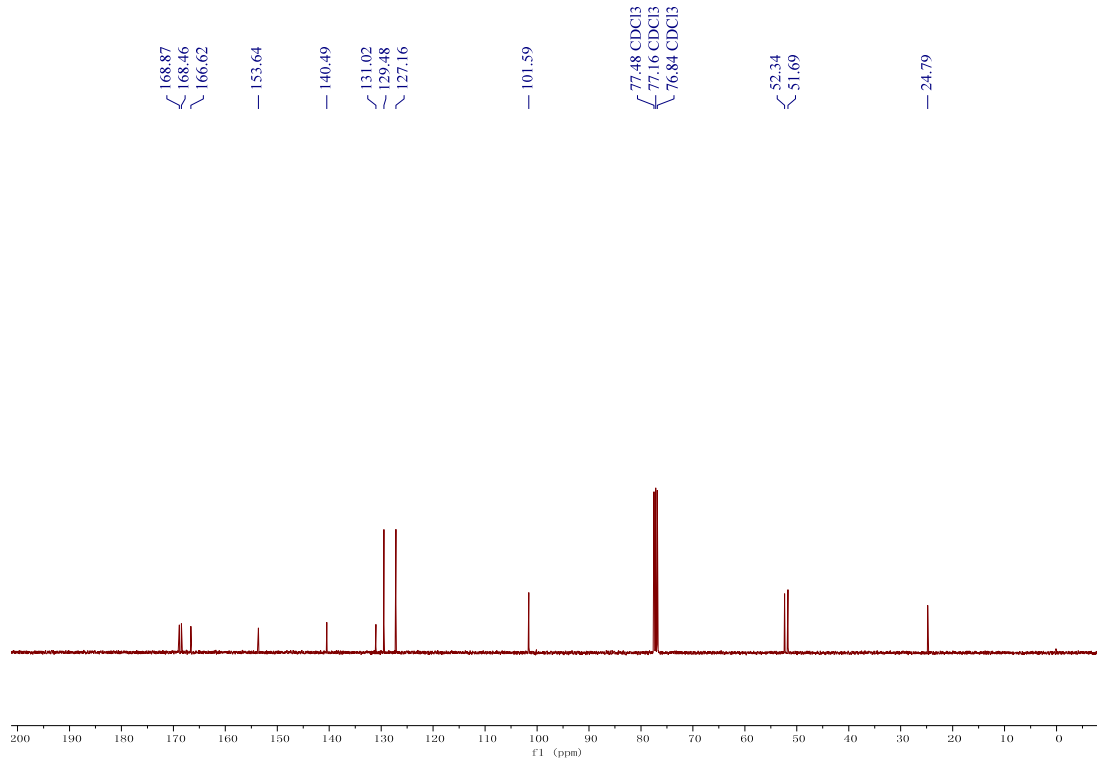
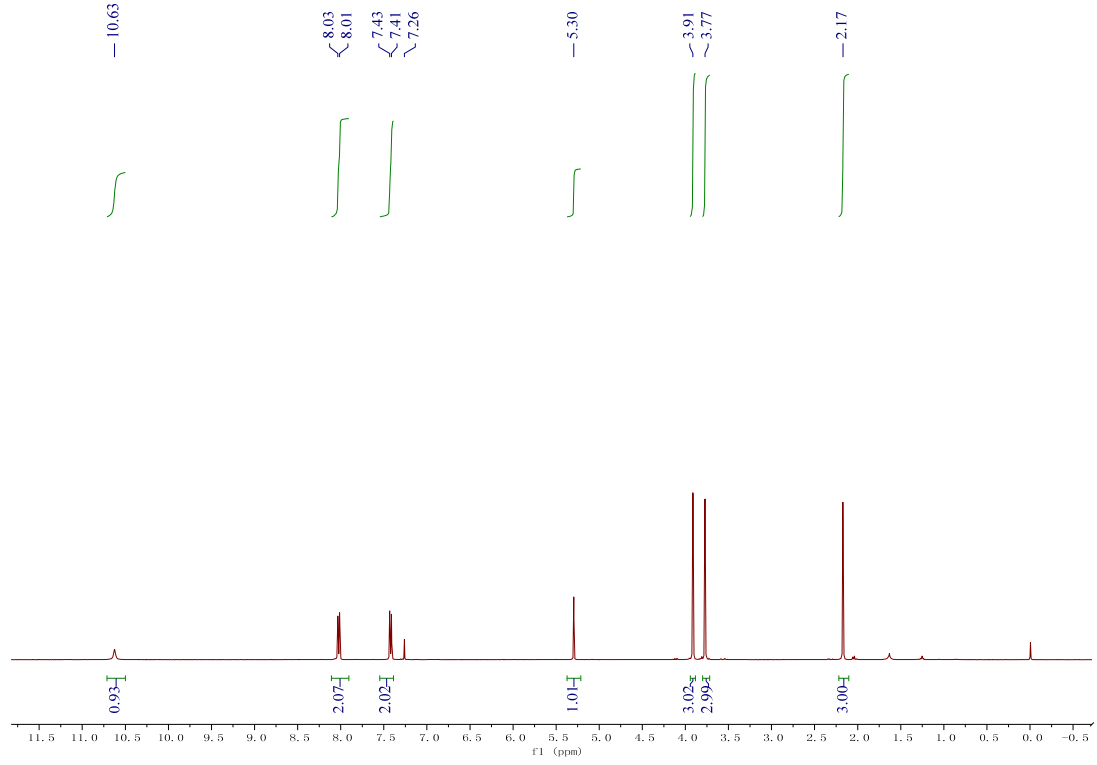
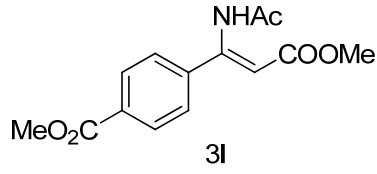


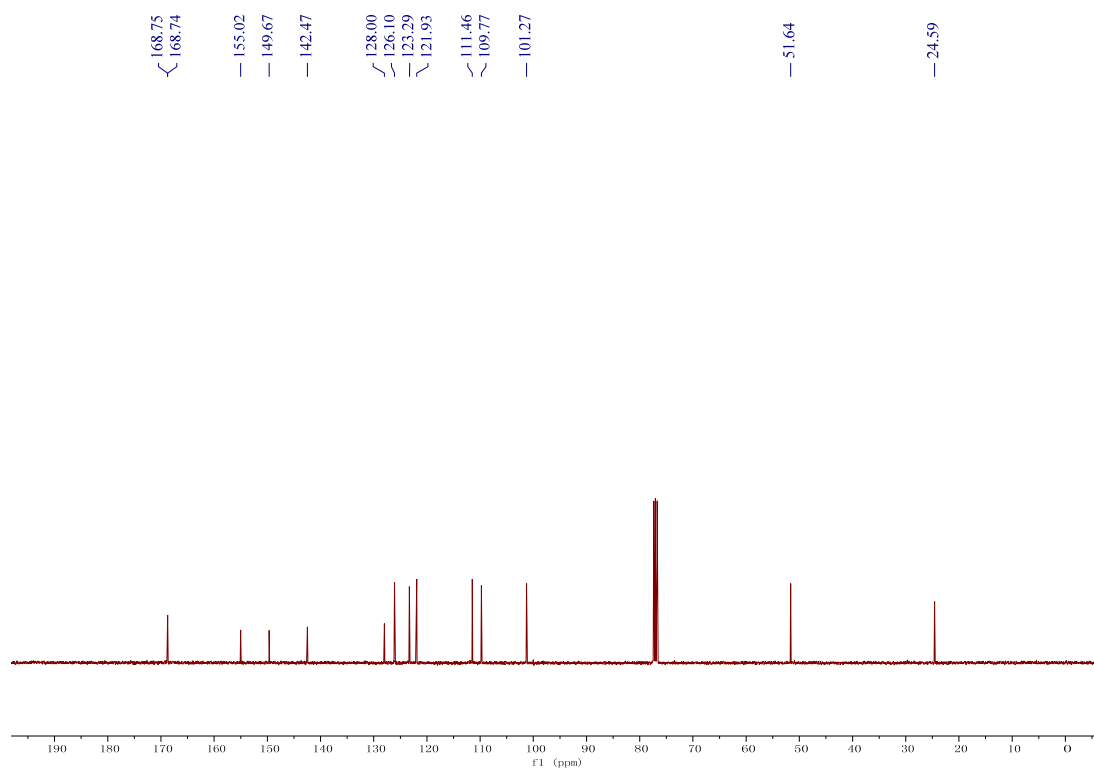
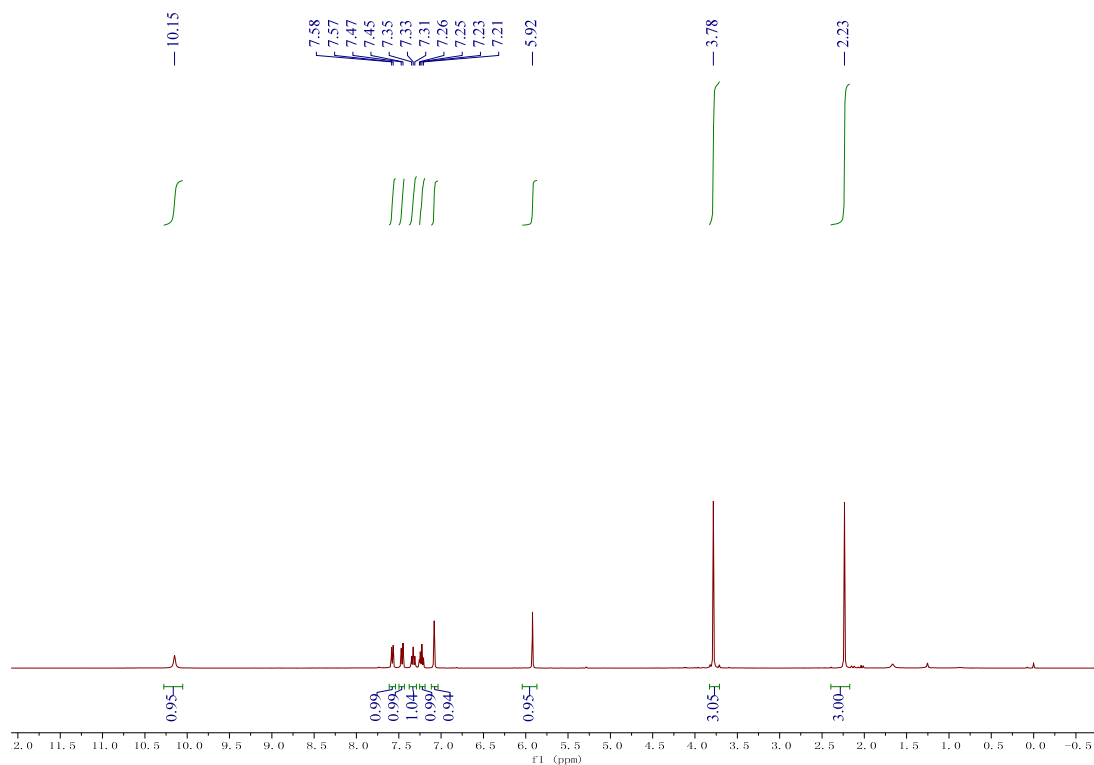
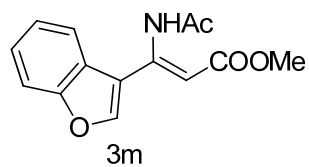


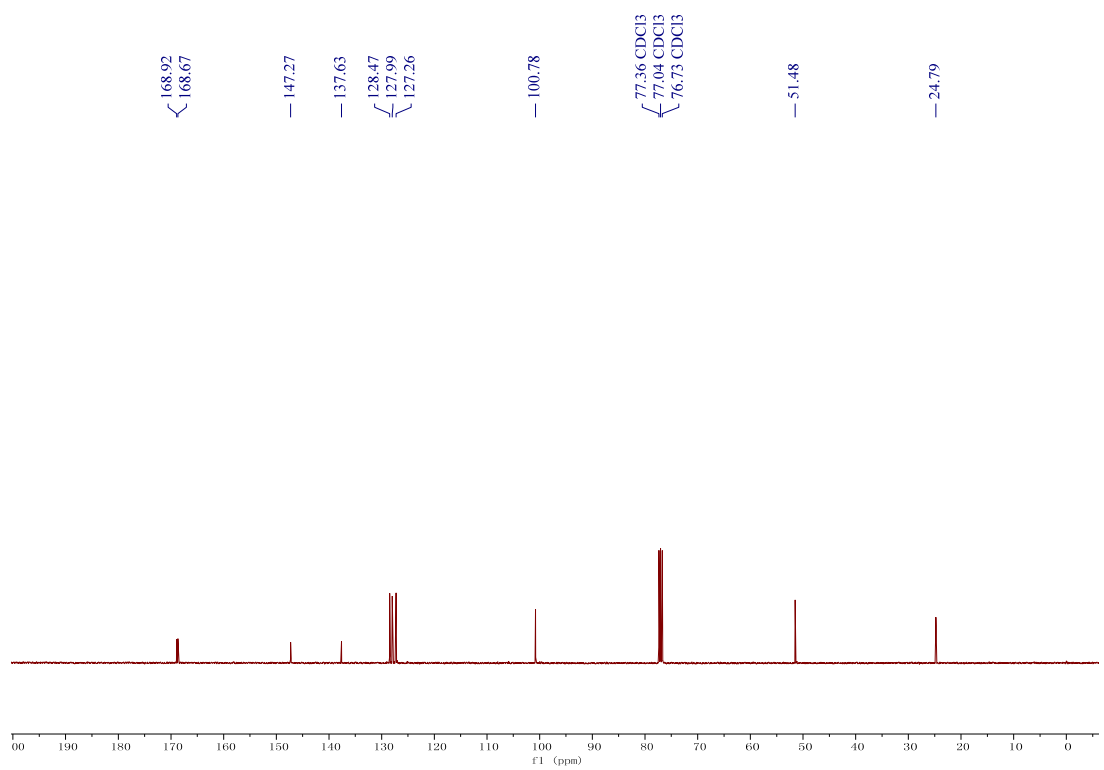
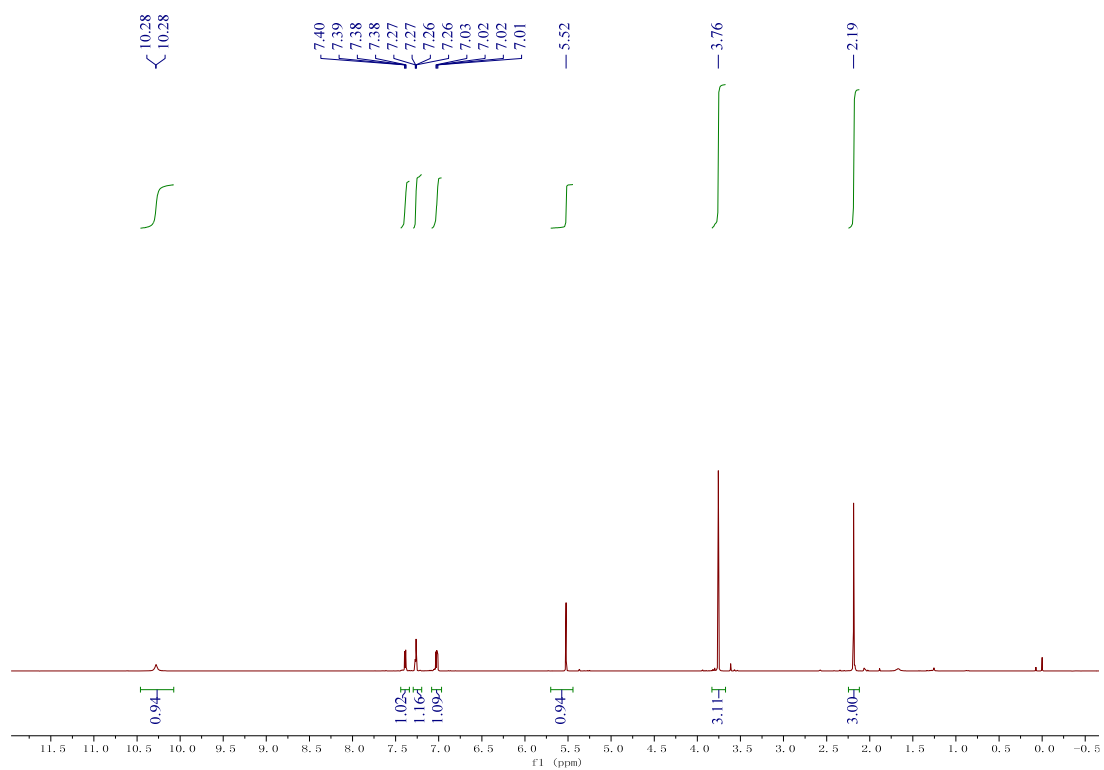
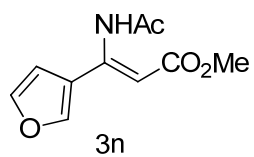


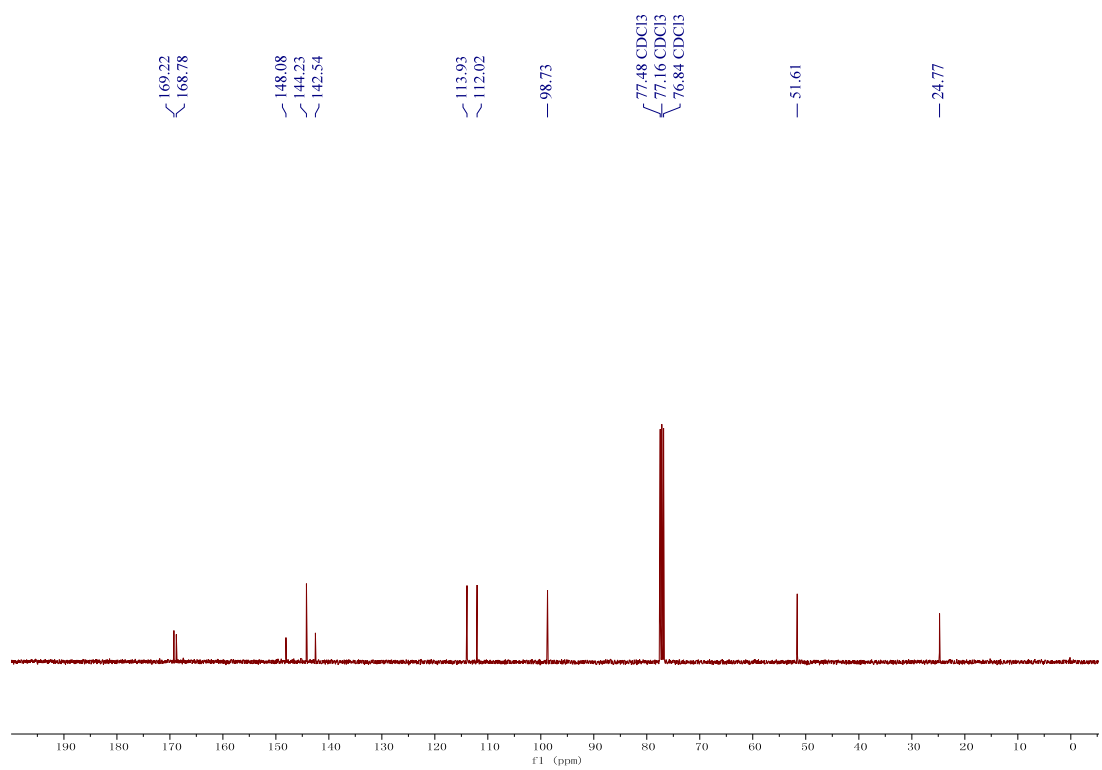
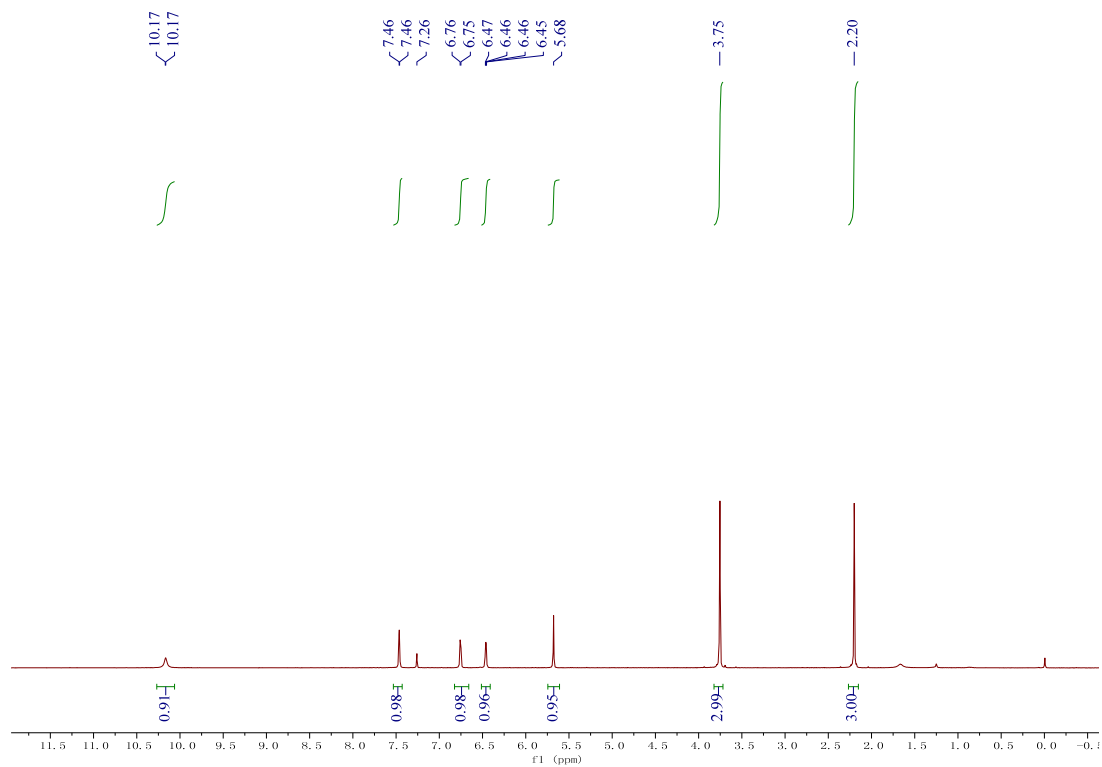
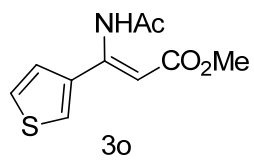


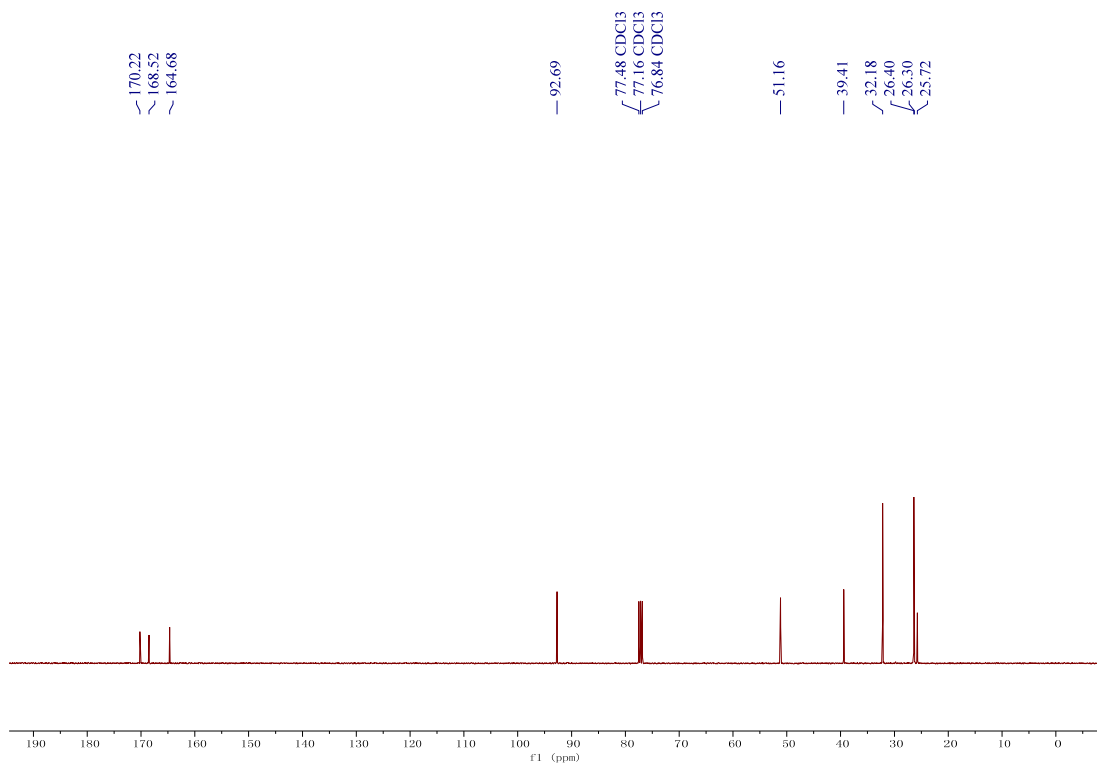
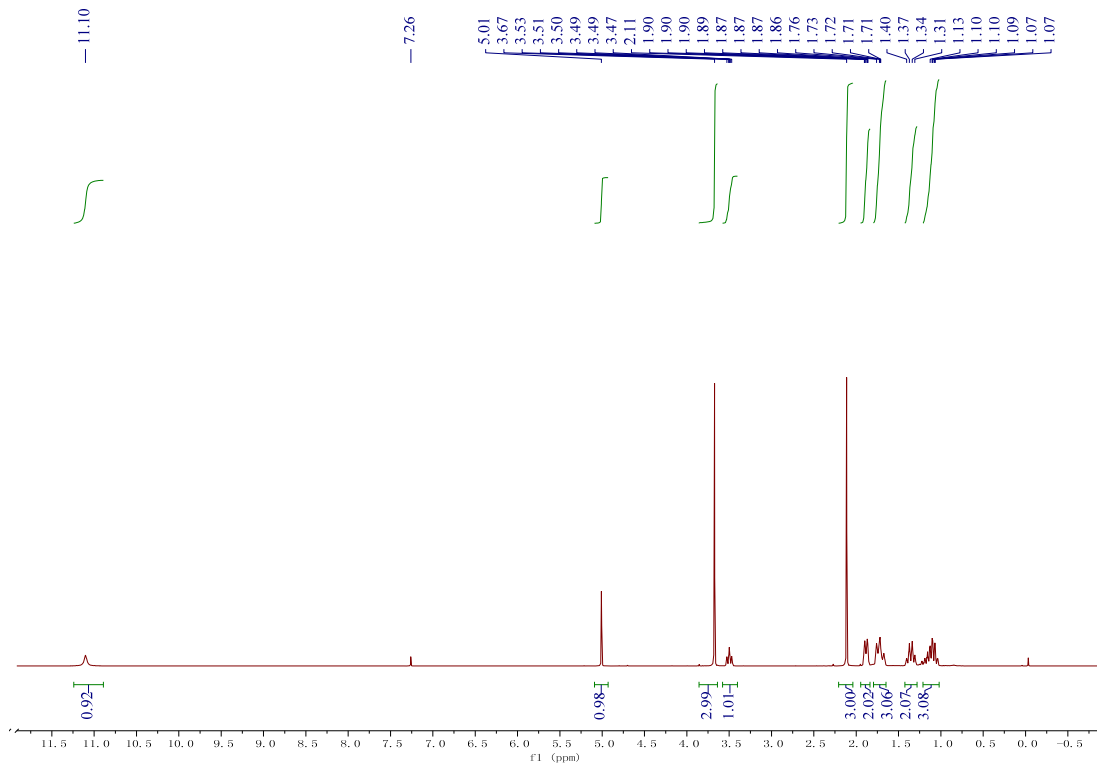
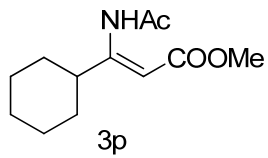


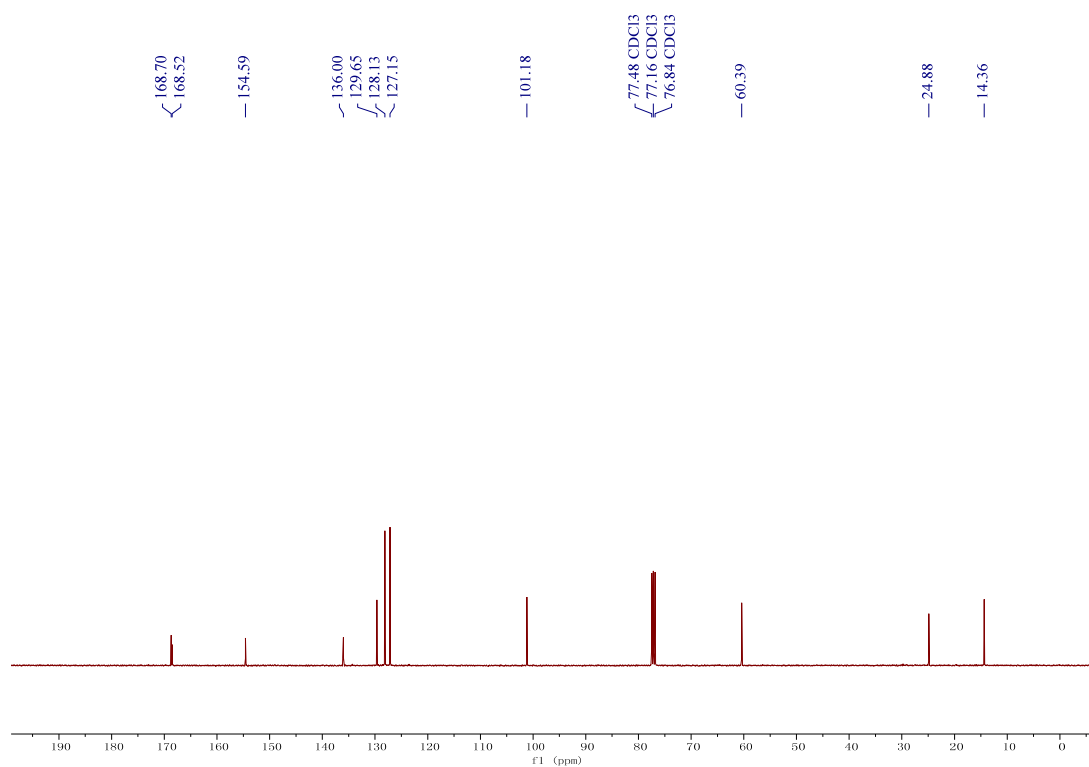
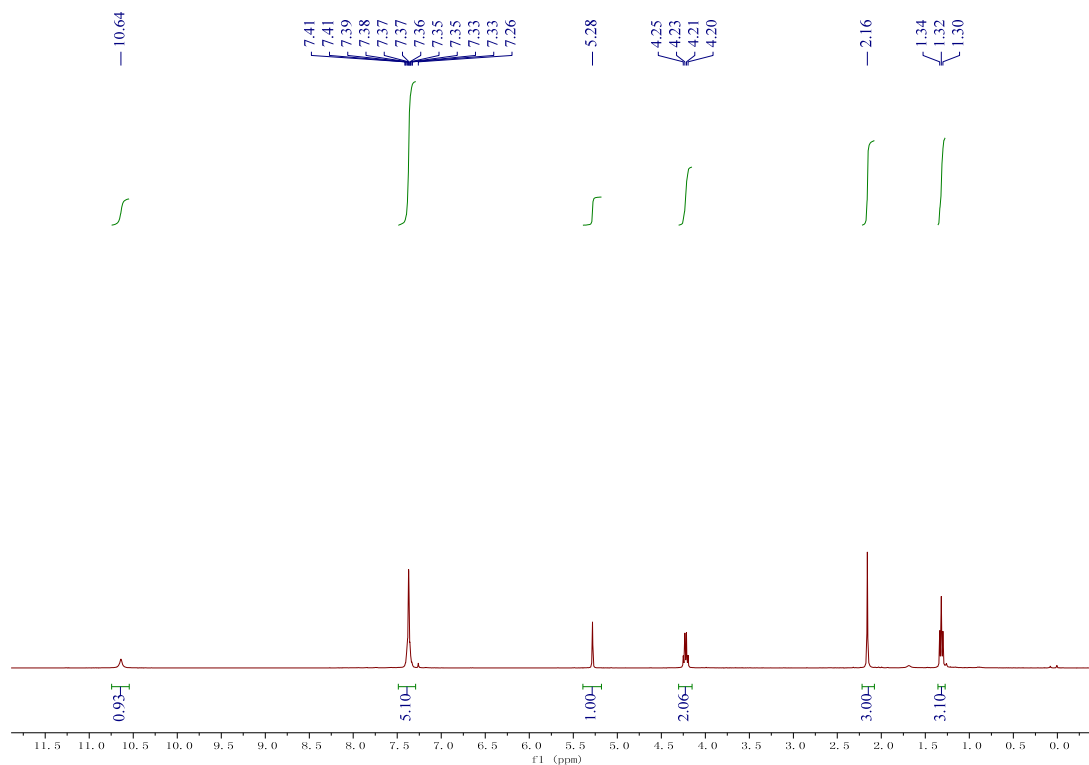
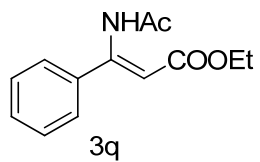


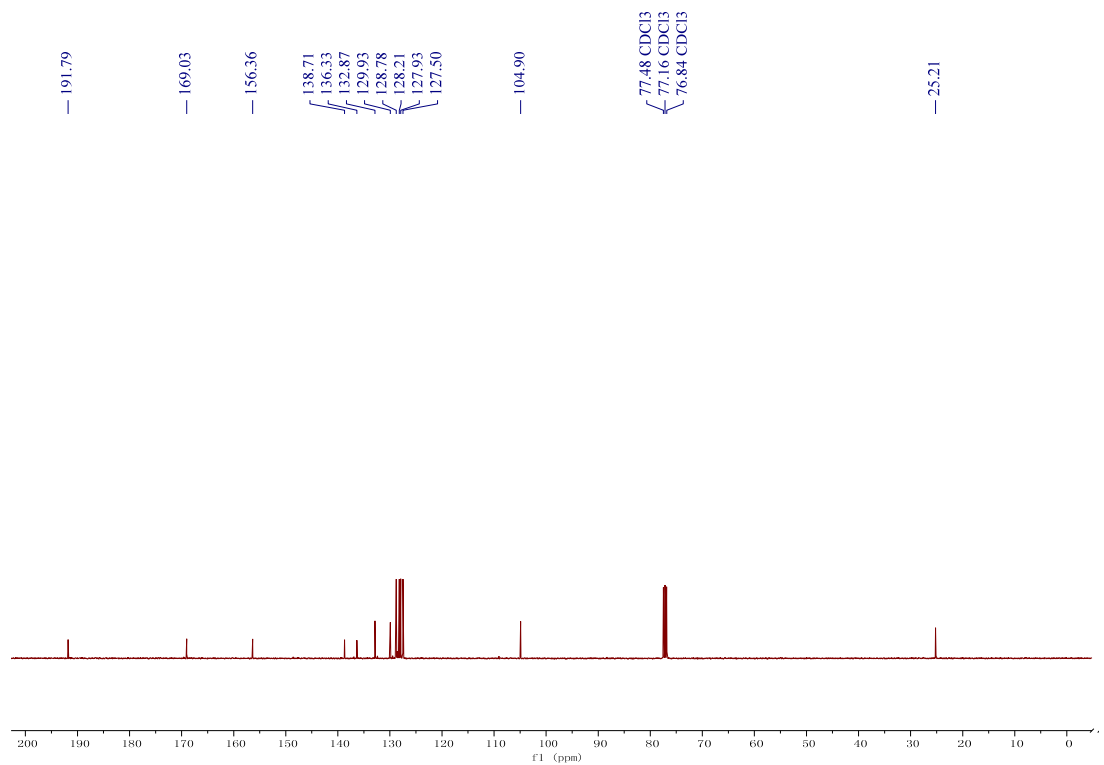
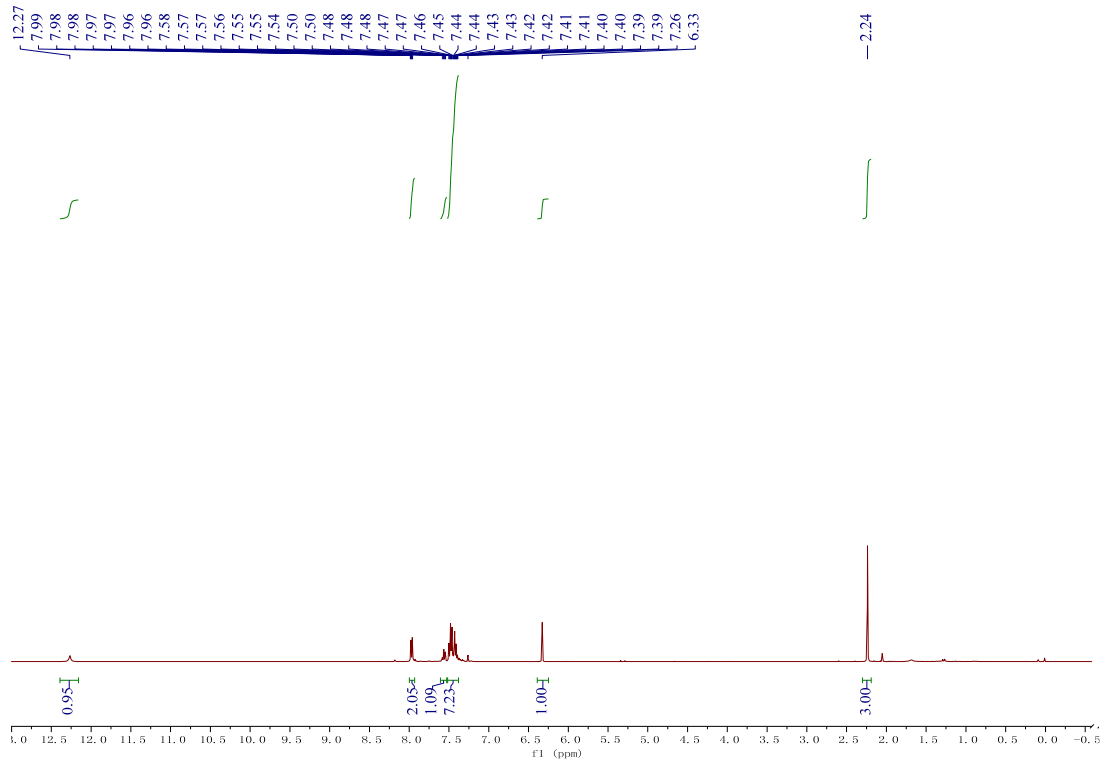
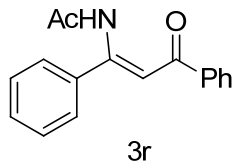


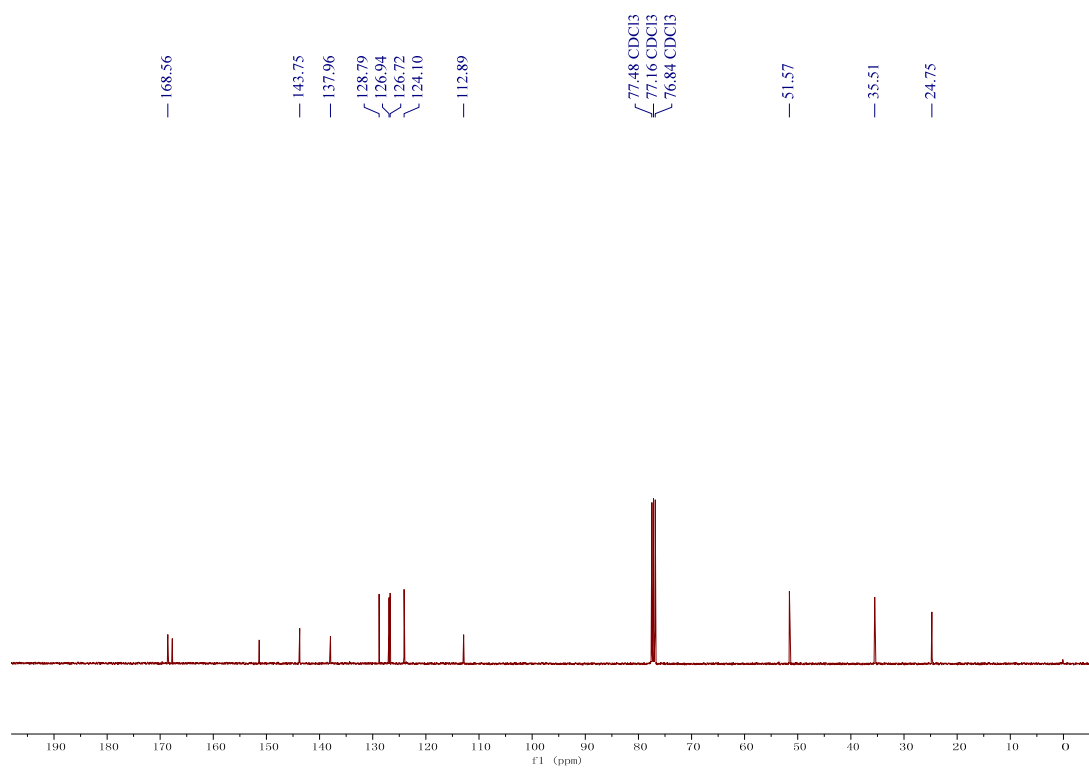
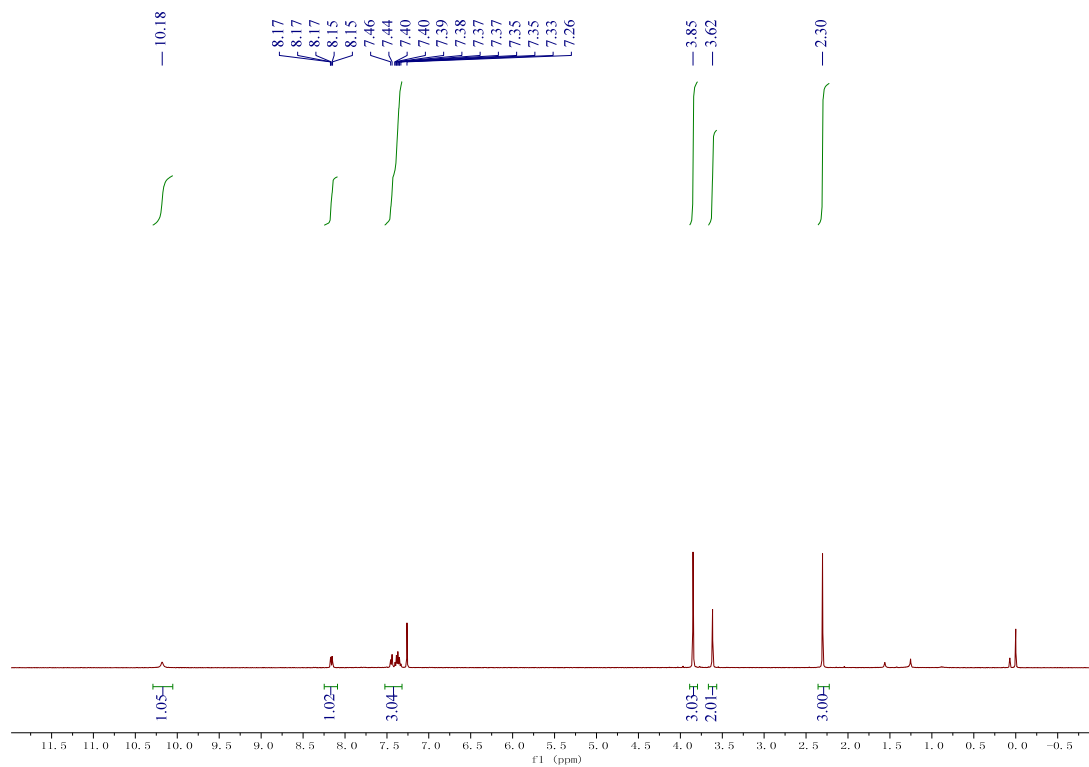
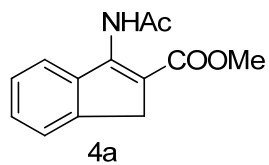


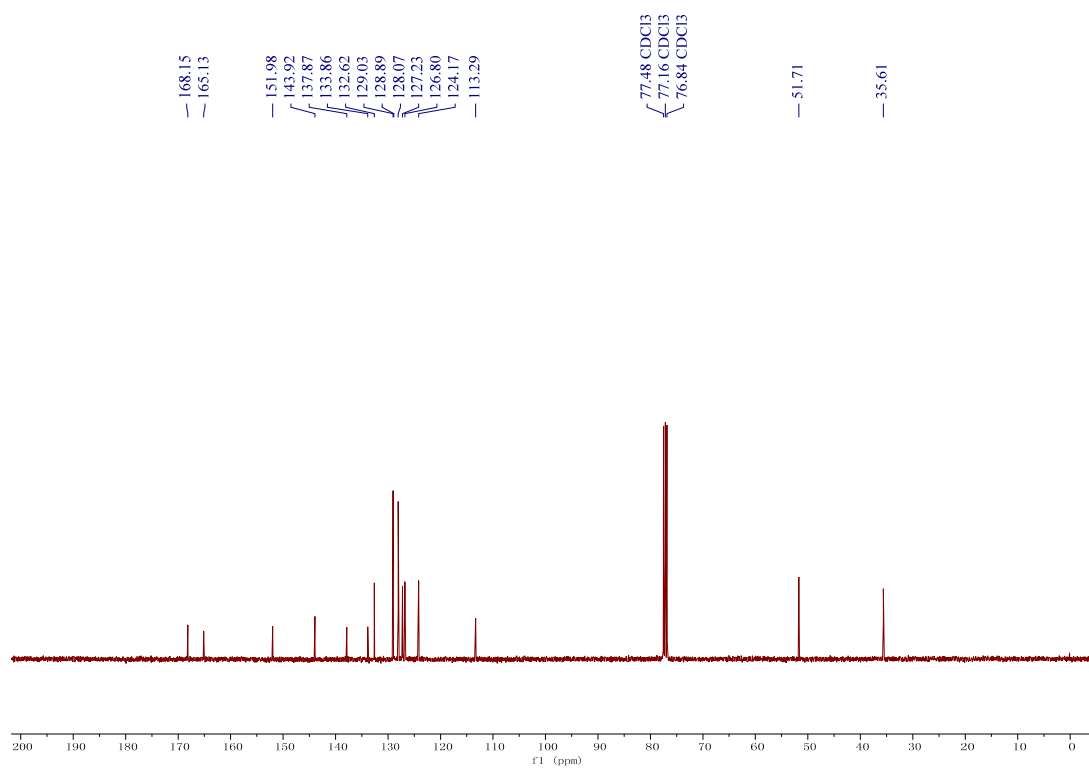
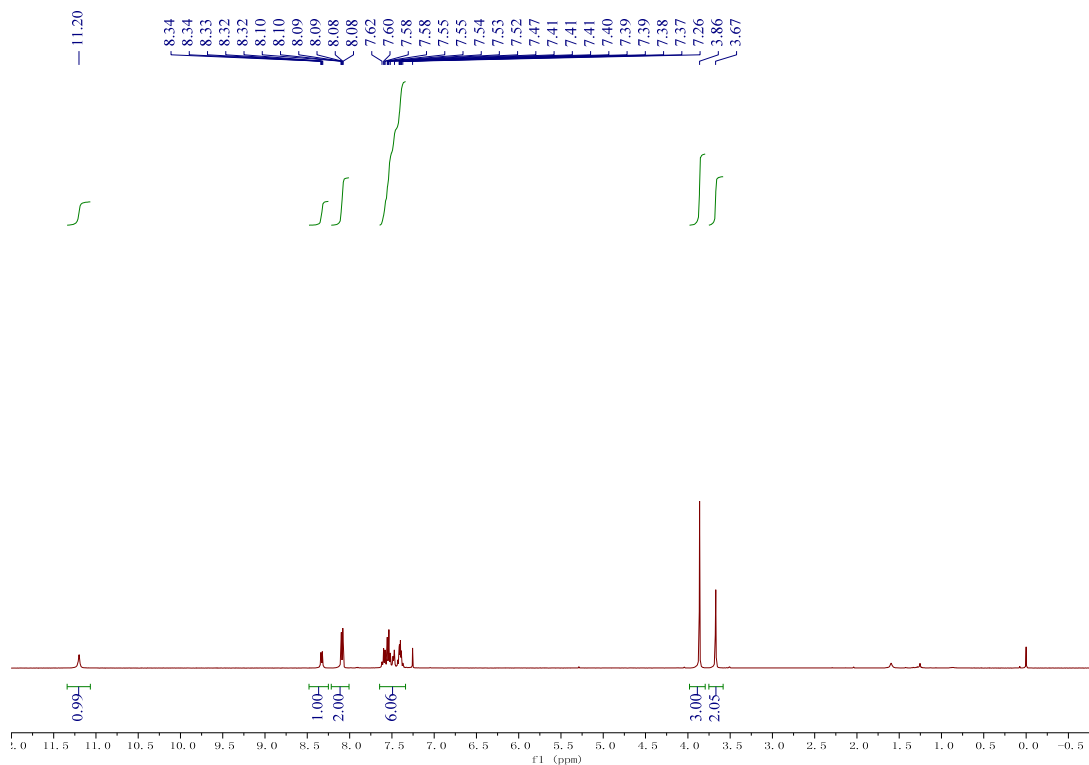
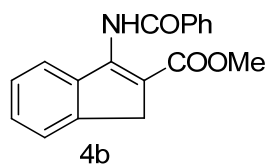


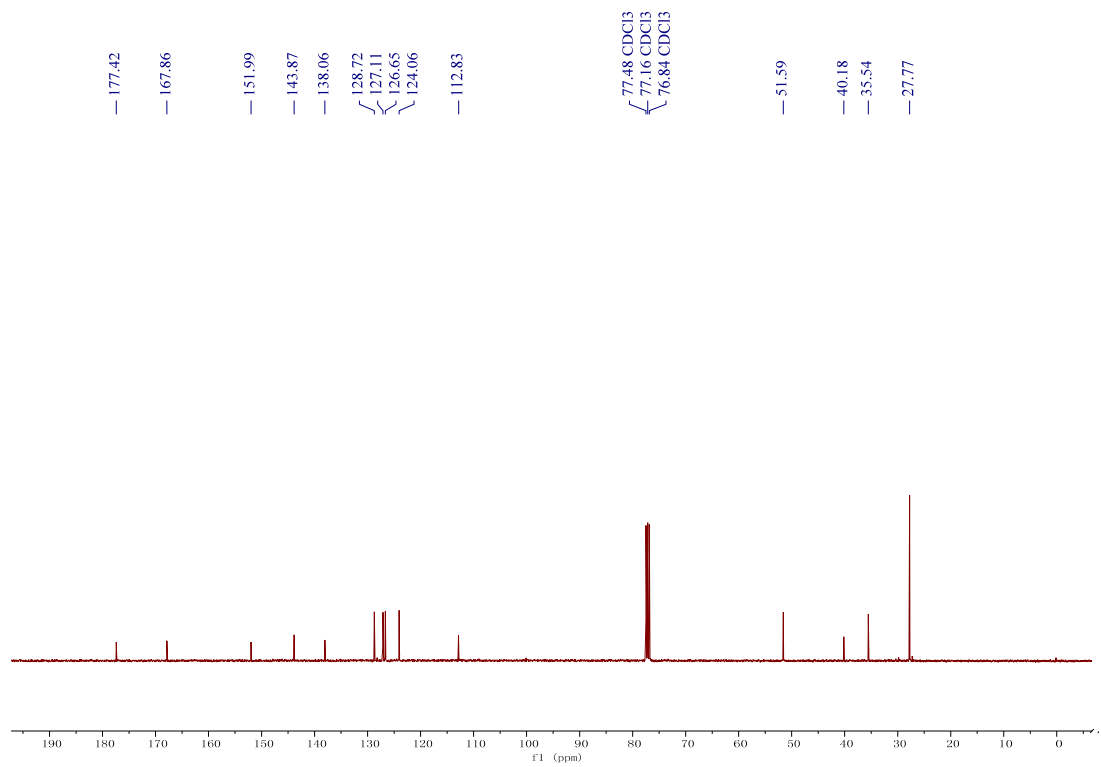
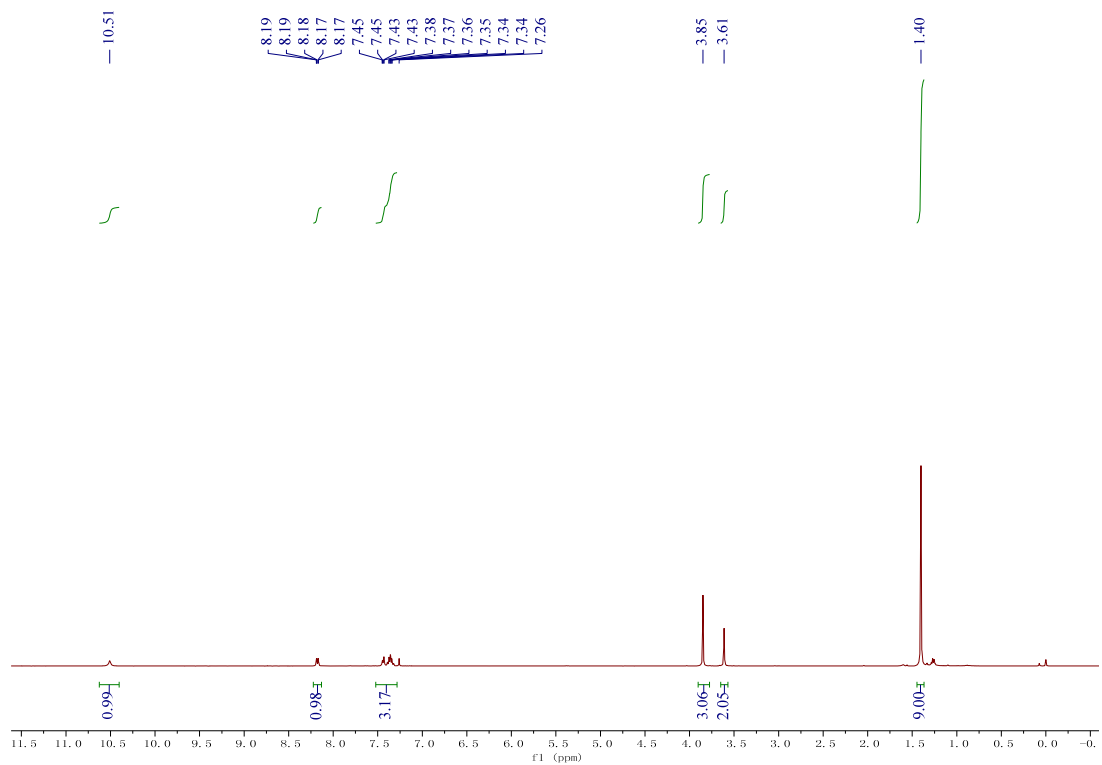
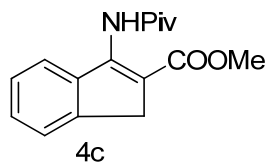


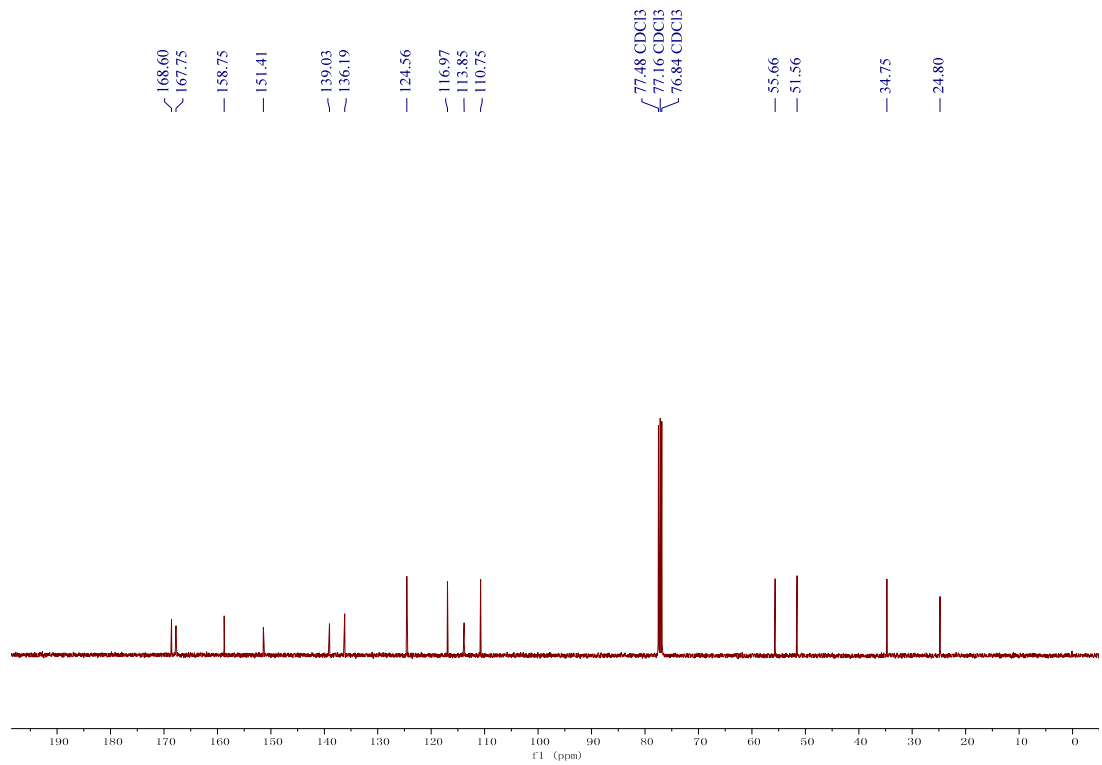
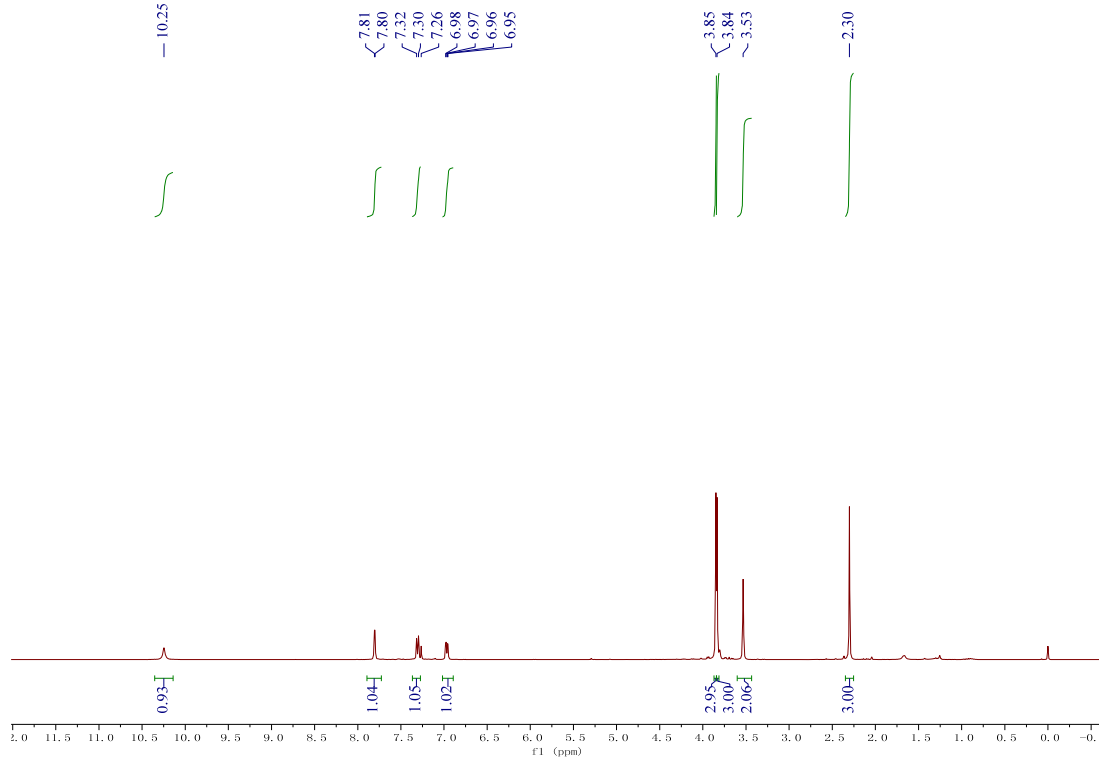
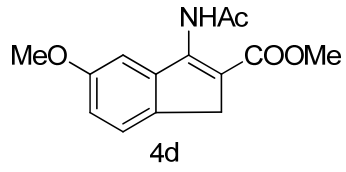


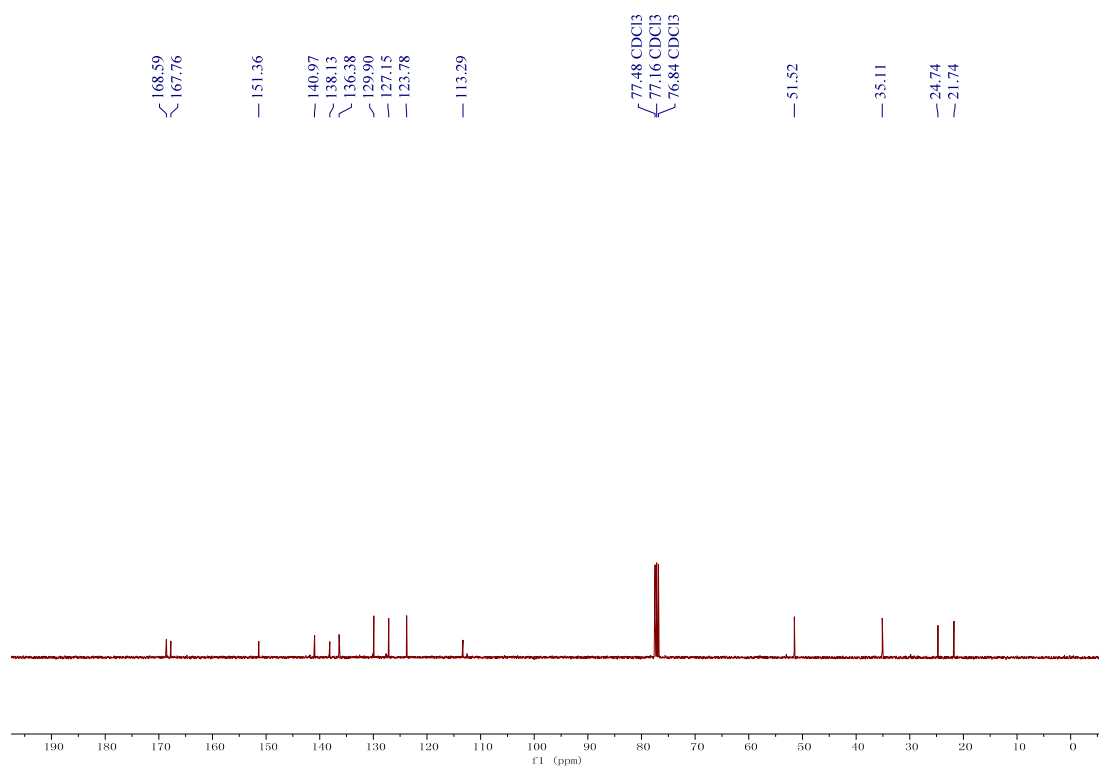
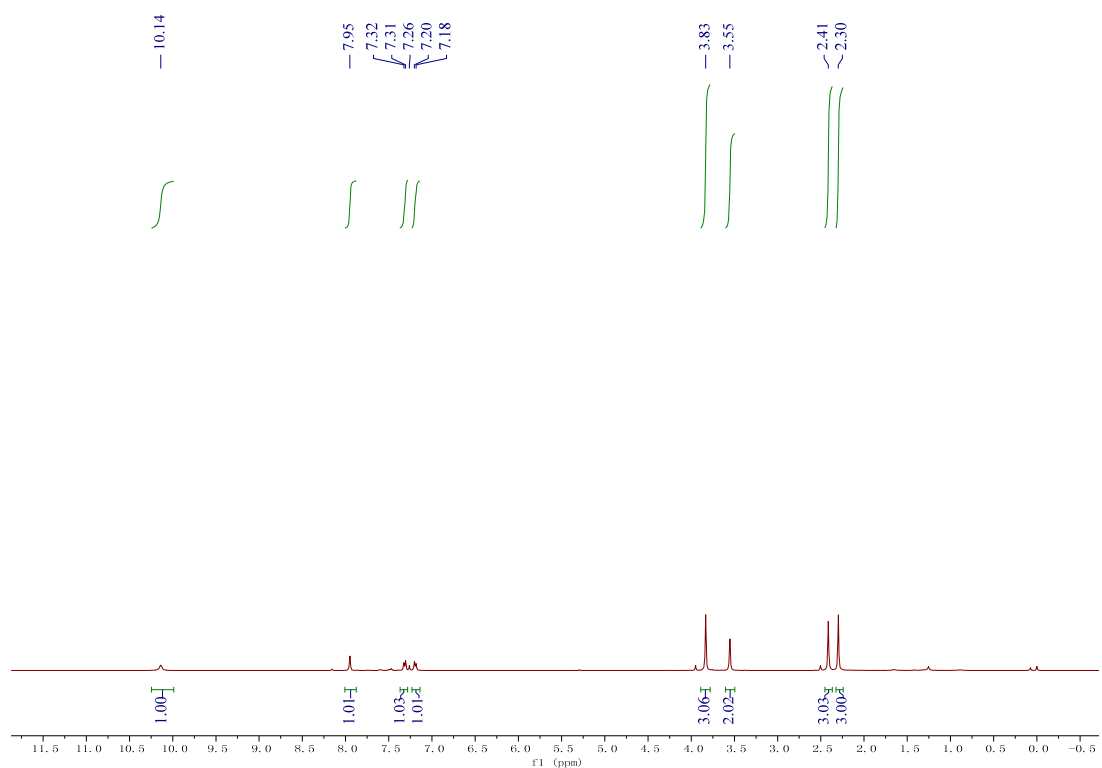
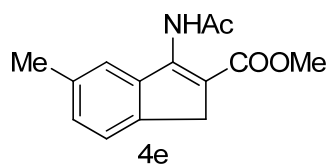


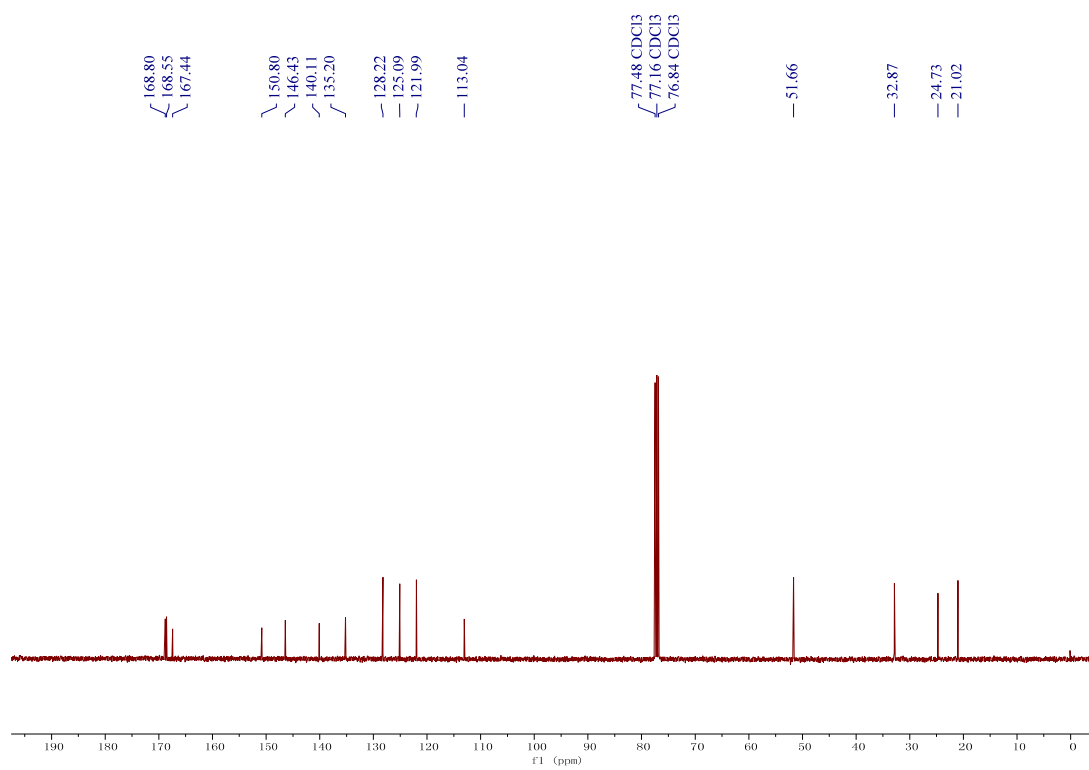
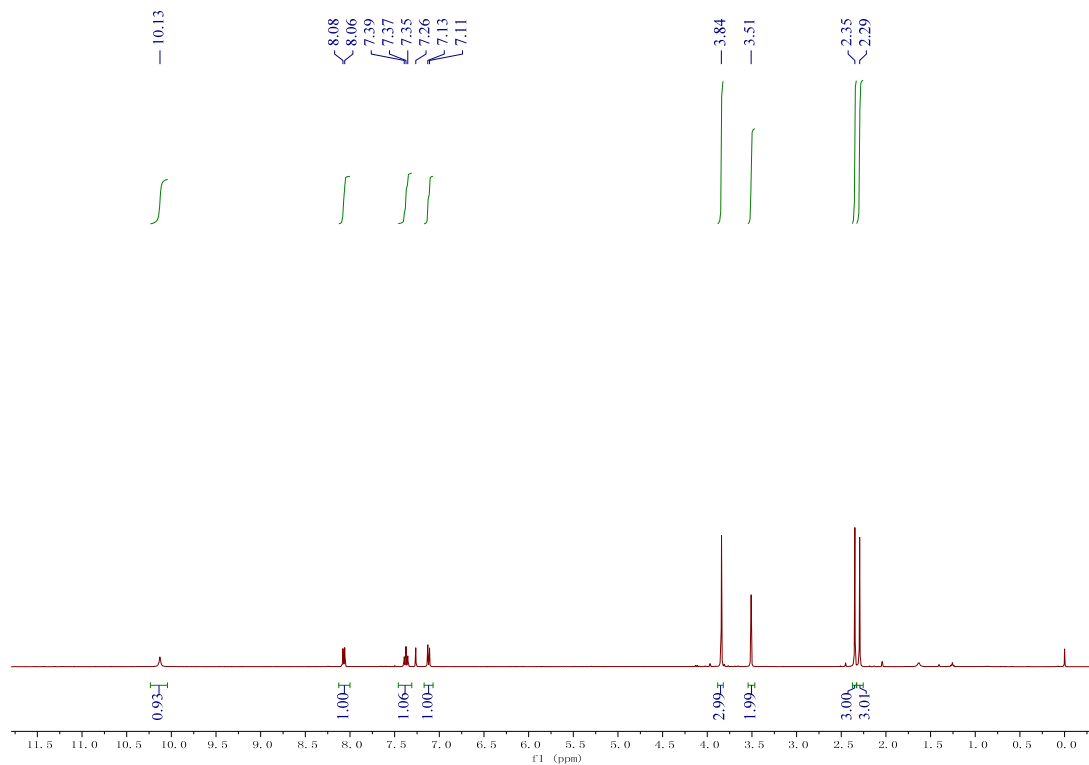
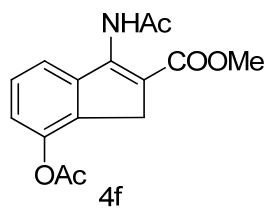


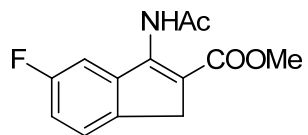




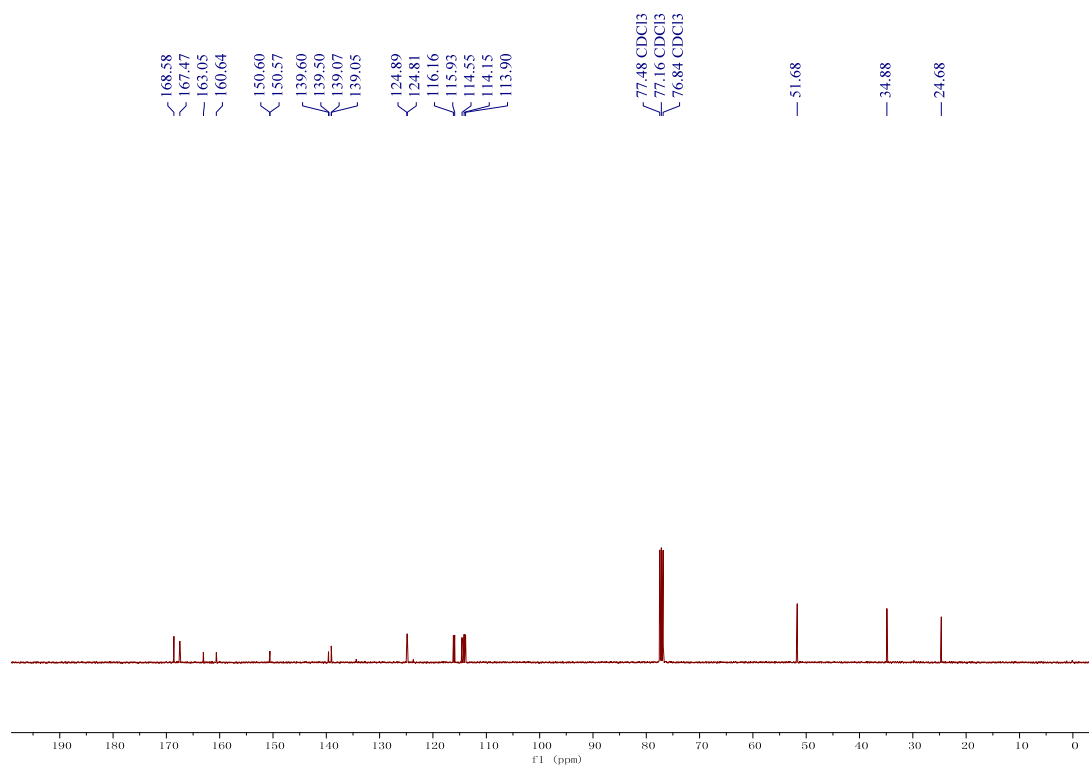
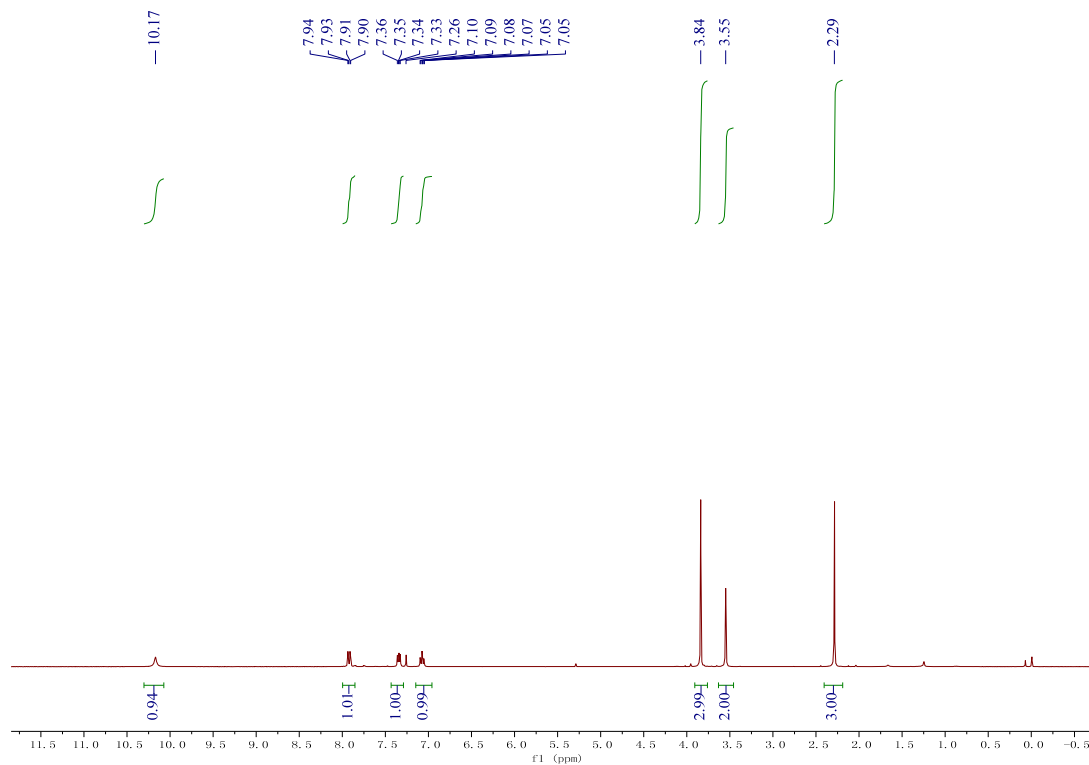


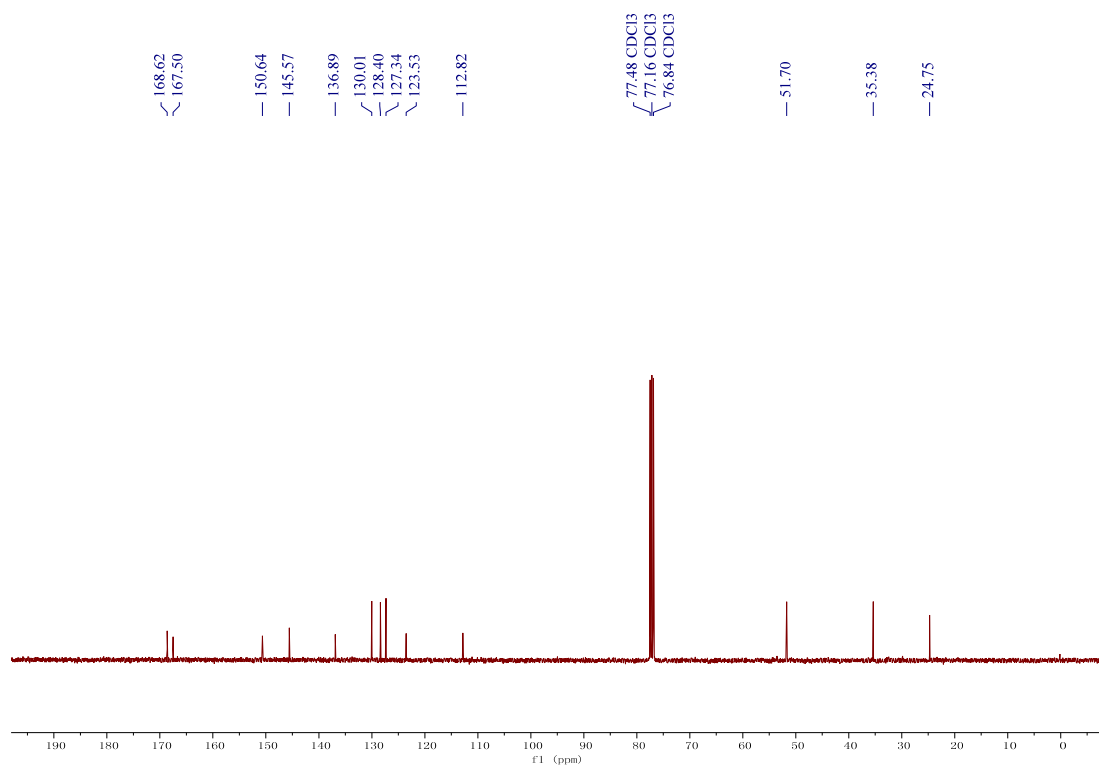
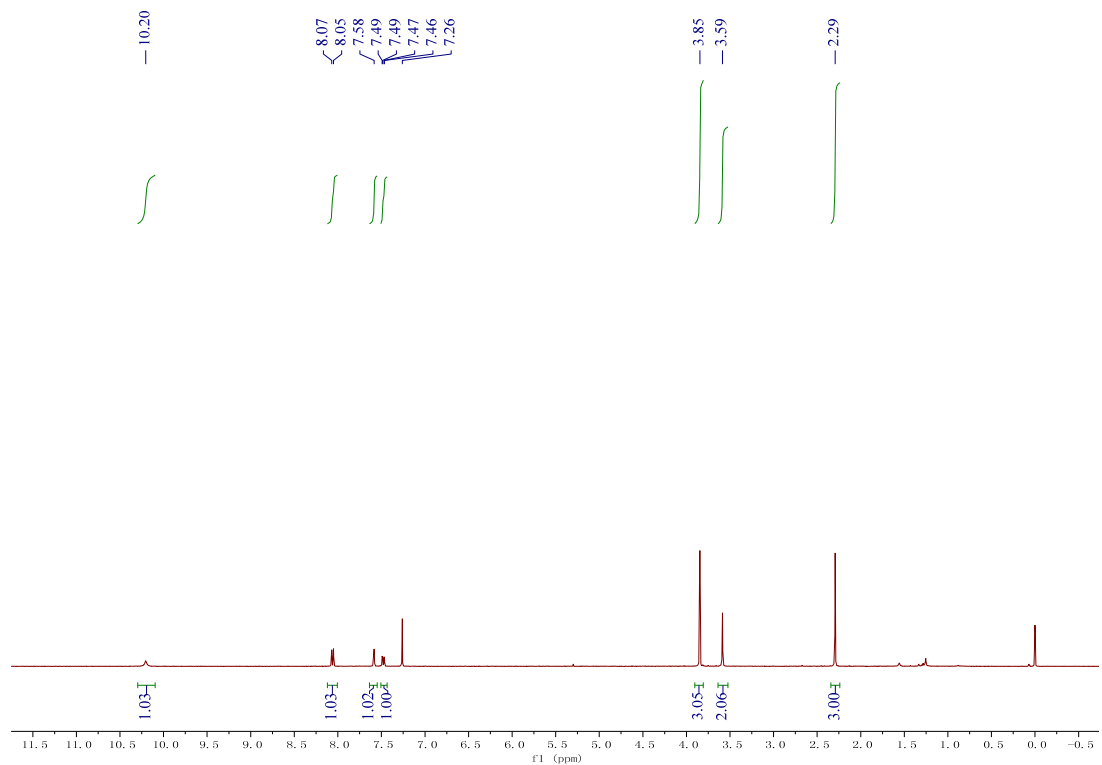
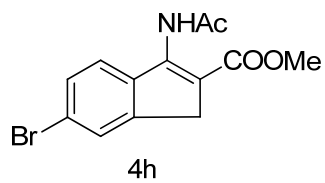


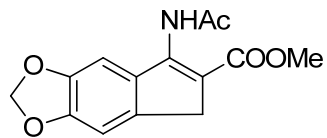




4g







4i

