SUPPORTING INFORMATION

for the article entitled

Synthesis and Characterization of a Cyclic Vinylpalladium(II) Complex: Evidence of Vinylpalladium Species As the intermediate in the Catalytic Direct Olefination Reaction of Enamides

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Supporting Information

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General Methods:

All commercially obtained reagents for the cross-coupling reaction were used as received: Anhydrous DMSO and acetic acid were obtained from Sigma-Aldrich and used as received. DMSO-d_6 and $CDCl_3$ were obtained from Cambridge Isotope Laboratories, Inc. and were used as received. The enamide substrates were prepared according to reported references.[1] All cross-coupling reactions were performed under 1 atm O_2. Thin-layer chromatography (TLC) was conducted with Merck 60 F254 precoated silica gel plate (0.2 mm thickness) and visualized with UV and potassium permanganate staining, followed by heating on a hot plate. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. ^{1}H NMR spectra were performed on a Bruker Advance 300, 400 and 500 NMR spectrometer and are reported in ppm downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ = 7.26, singlet) or dimethyl sulfoxide-d_6 (δ = 2.50, singlet). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C NMR spectra were recorded on a Bruker Advance-300 (75 MHz), Bruker Advance-400 (100 MHz) or Bruker Advance-500 (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.23 ppm, DMSO-d_6 at 39.52 ppm). Regioselectivity of the cross-coupling was determined by NMR analysis of the crude product. IR spectra were recorded as thin films on NaCl plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectral analysis (HRMS) was performed on Waters Q-Tof Permies Mass Spectrometer.

Mechanism Investigation:

Procedure:

(1) A dried round bottom flask was charged with *N*-[1-(naphthalene-2-yl)vinyl]acetamide (1 equiv, 212 mg), $Pd(OAc)_2$ (1 equiv, 225 mg) and DMSO-d_6 (0.5 mL). The mixture was stirred at room temperature for 10 hours. The solution was filtered via a filter paper and washed with dichloromethane (2 mL). To the filtrate was added diethyl ether (100 mL) slowly. Brown floccules were deposited and isolated by filtration. Crystal suitable for X-ray analysis was prepared by recrystallization. The structure was shown as Figure **1**. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.20 (s, 1H), 7.89-7.94 (m, 4H), 7.49-7.53 (m, 3H), 5.78 (s, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.0, 134.1, 133.1, 132.8, 132.3, 128.4 128.3, 128.0, 127.1, 126.8, 125.8, 125.4, 122. 9, 21.9. FTIR (NaCl, cm^{-1}): 3415, 3053, 2985, 2304, 1647, 1550, 1421, 1265, 894.

[1] (a) Burk, M. J.; Casy, G.; Johnson, N. B. *J. Org. Chem.* **1998**, *63*, 6084. (b) Matsubara, R.; Nakamura, Y.; Kobayashi, S. *Angew. Chem. Int. Ed.* **2004**, *43*, 1679. (c) Zhao, H.; Vandenbossche, C. P.; Koenig, S. G.; Singh, S. P.; Bakale, R. P. *Org. Lett.* **2008**, *10*, 505.

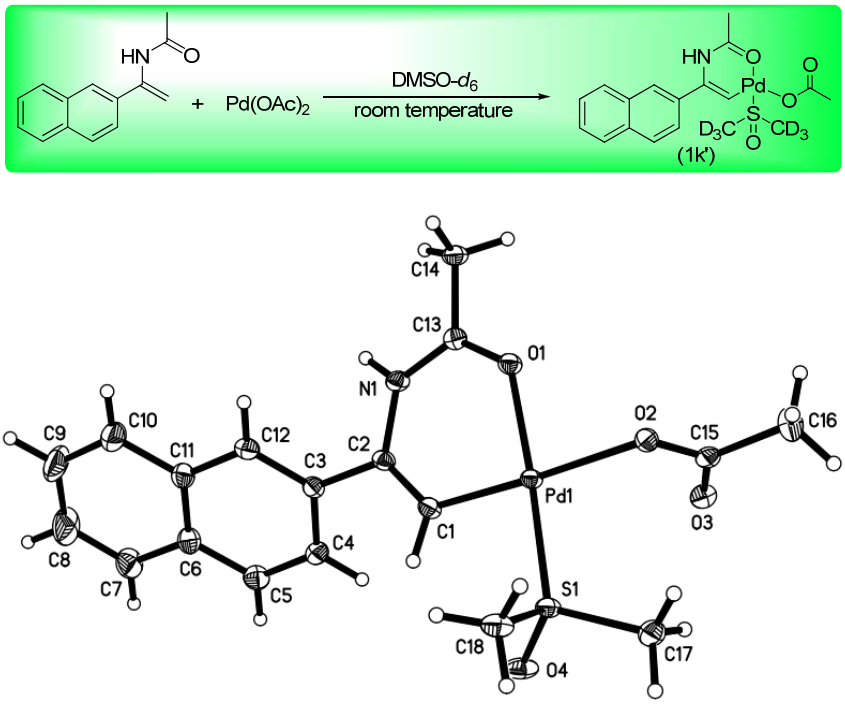
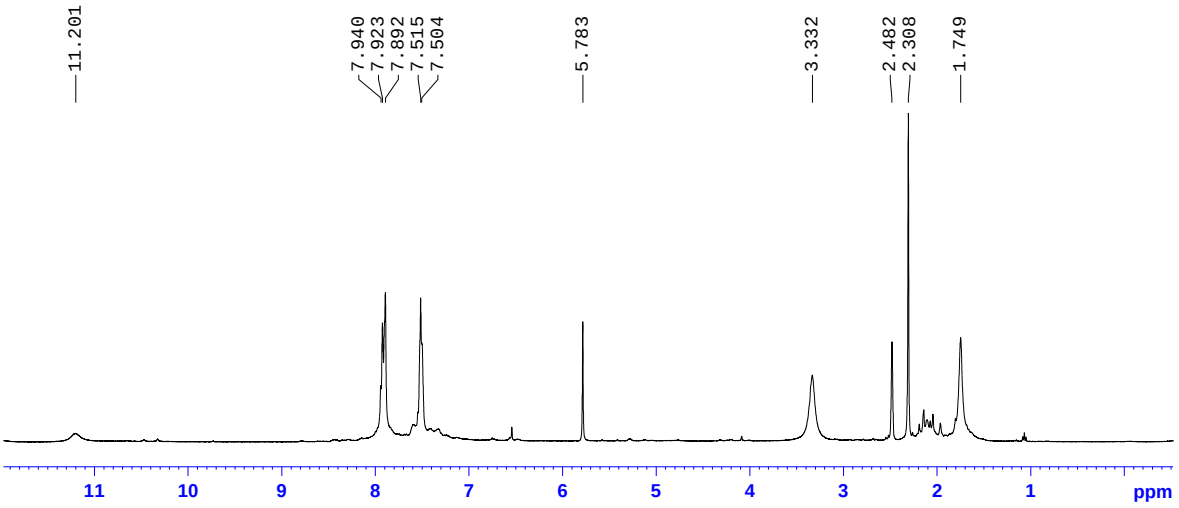
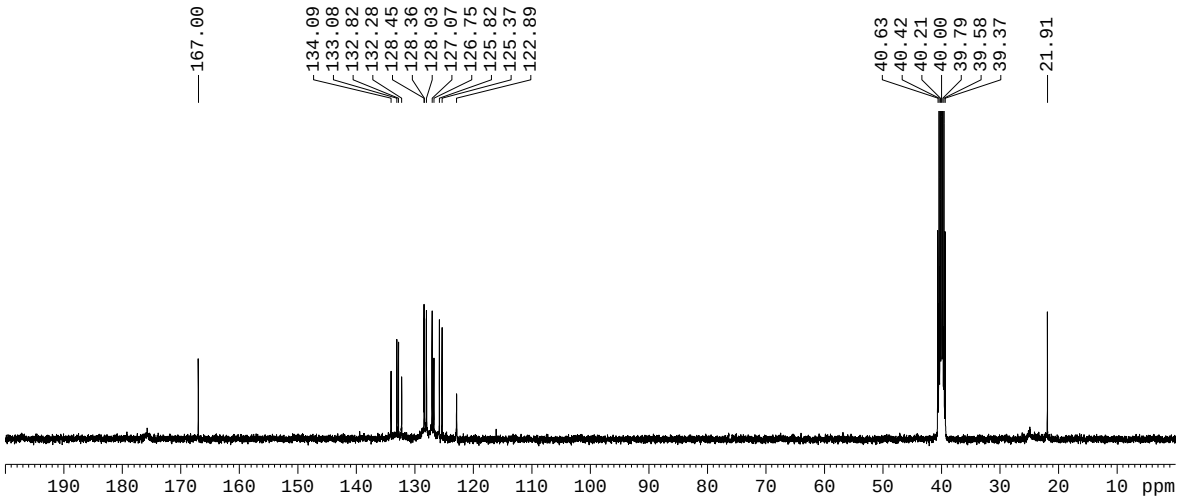


Figure 1. ORTEP of palladacycle **1k′**. Thermal ellipsoidsmare set at 50% probability.





^{1}H, ^{13}C NMR spectroscopy of compound **1k′**

(2) A dried round bottom flask was charged with *N*-[1-(naphthalene-2-yl)vinyl]acetamide (1 equiv, 212 mg), $Pd(OAc)_2$ (1 equiv, 225 mg) and DMSO (0.5 mL). The mixture was stirred at room temperature for 10 hours. The solution was diluted with 5 mL dichloromethane and washed with water (twice, 5 mL) and brine (5 mL) in sequence. The organic layer was dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure. A brown solid was obtained and crystal suitable for X-ray analysis was prepared by recrystallization. The structure was shown as Figure **2**. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.27 (s, 1H), 7.92-8.00 (m, 4H), 7.50-7.57 (m, 3H), 5.90 (s, 1H), 2.35 (3H). ^{13}C NMR (100 MHz, DMSO-d_6): 166.8, 133.7, 133.1, 132.9, 131.5, 128.5, 128.0, 127.1, 126.8, 125.7, 125.5, 40.9, 21.9. FTIR (NaCl, cm^{-1}): 3018, 1600, 1529, 1431, 1265, 1215, 1122, 1008.

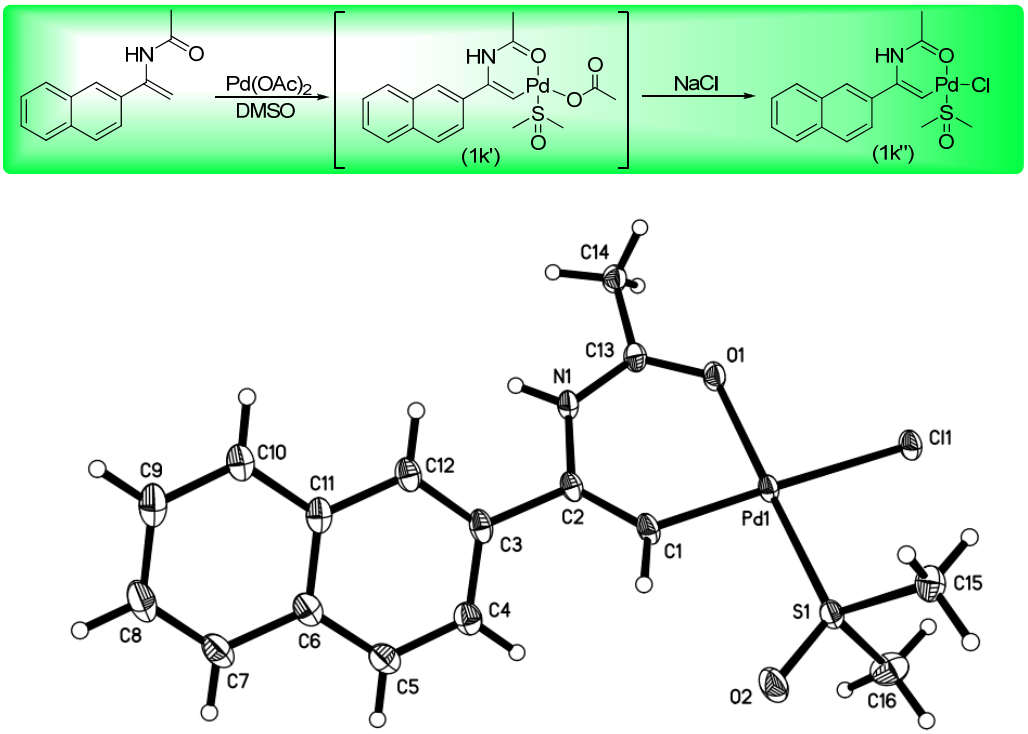
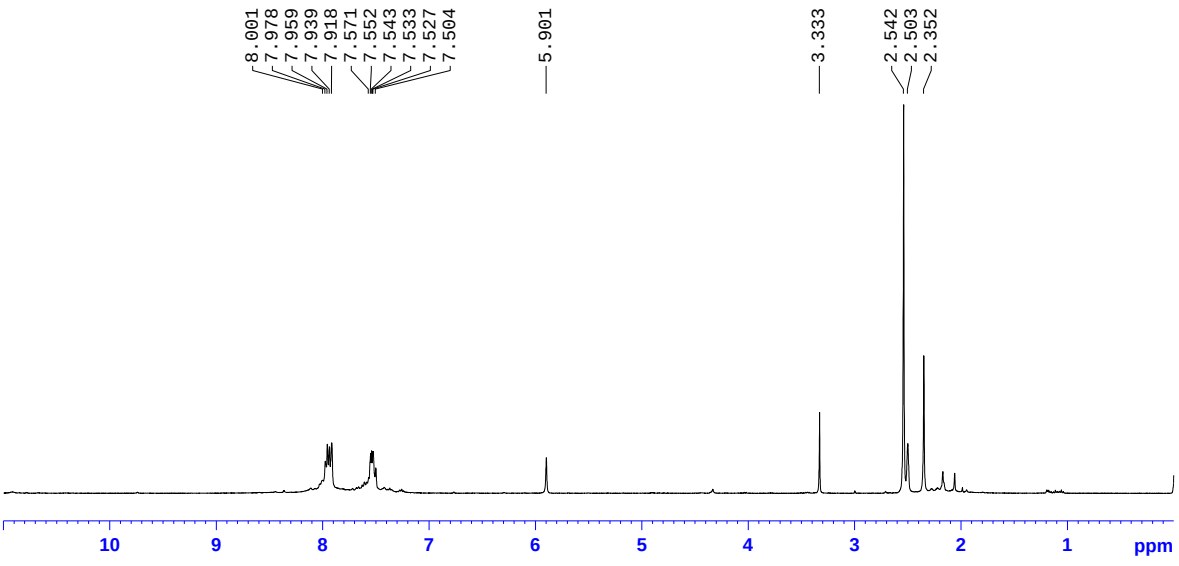
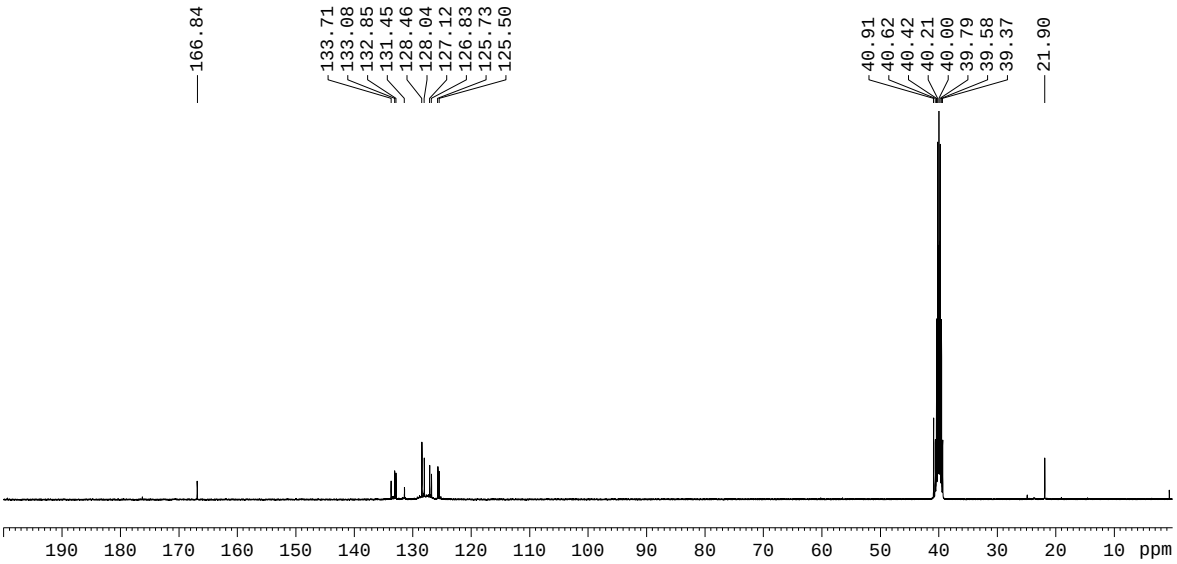


Figure 2. ORTEP of palladacycle **1k″**. Thermal ellipsoidsmare set at 50% probability.





^{1}H, ^{13}C NMR spectroscopy of complex **1k″**

(3) A dried round bottom flask was charged with the solid sample of **1k′** (1 equiv, 113.3 mg), sodium acetate (1 equiv, 20.5 mg), *tert*-butyl acrylate (1 equiv, 32 mg) and 0.5 mL of DMSO. The mixture was heated at 80 °C under an air atmosphere for 16 hours. After cooling down to room temperature, the reaction was diluted with chloroform (5 mL) and filtered. The filtrate was washed with water (twice, 5 mL) and brine (5 mL). The organic layer was dried with anhydrous $MgSO_4$ and the organic solvent was removed under reduced pressure. The crude product was purified by chromatography on silica gel, and compound **3k** was obtained in 53% yield.

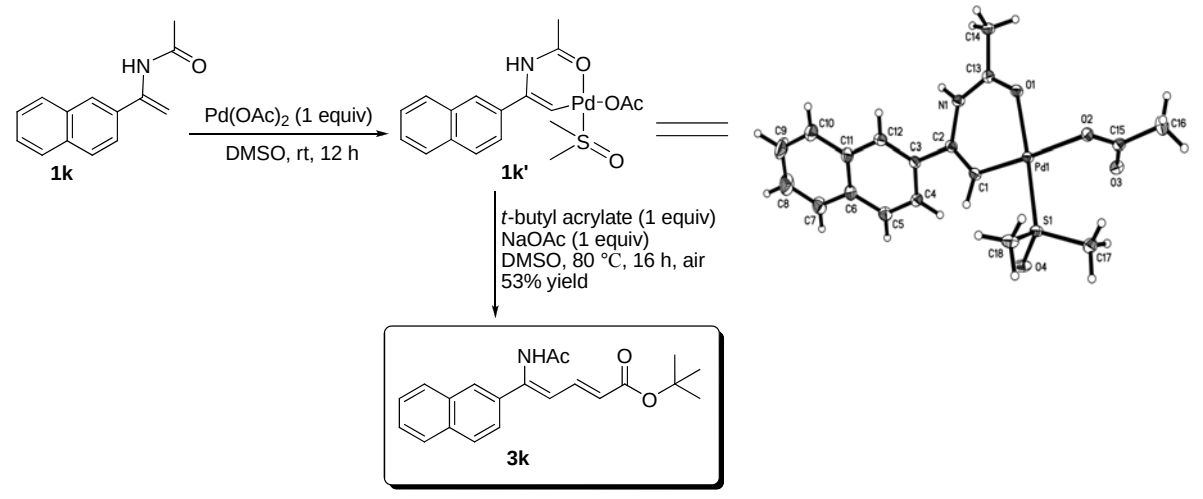


Figure 3. Evidence of vinylpalldacycle complex as intermediate for the direct olefination of enamide

NMR Study:

N-[1-(naphthalene-2-yl)vinyl]acetamide (0.1 mmol, 16.1 mg) in 0.5 mL DMSO-d_6 in an NMR tube was scanned at 25 °C with a Bruker Advance 400 NMR, and the ^{1}H NMR spectrum is shown as Figure 4-(a). The two signals at 5.17 and 5.69 ppm were assigned to the two terminal alkenyl protons respectively. Palladium(II) acetate (0.11 mmol, 1.1 equiv, 24.7 mg) was added into the solution and stirred for 10 hours at 25 °C, the mixture was checked again with the same Bruker Advance 400 NMR. It was found that one of the signal corresponding to the alkenyl protons disappeared from the spectrum almost completely (Figure 4-(b)). It was noted that a slight downfield shift of the acetyl methyl group from 2.07 to 2.34 ppm occurred (see Figure 4-(b)). The new complex was isolated as a solid *via* deposition with dry diethyl ether. Crystal suitable for X-ray analysis was prepared by recrystallization and a six-membered vinylpalladium cyclic intermediate (**1k′**) was unveiled. (Figure 4-(c)) Subsequently, to the mixture was introduced *tert*-butyl acrylate (0.10 mmol, 1.0 equiv, 12.8 mg) and heated at 80 °C for another 16 hours. The desired product **3k** (*ter*t-butyl 5-acetamido-5-(naphthalen-2-yl)penta-2,4-dienoate) was formed (Figure 4-(d)). The two geometric isomers of the desired product were separated by column chromatography. (Figure 4-(e) and Figure 4-(f))

Proposed Mechanism for the Palladium(II) Acetate Catalyzed Catalytic Coupling of Enamides with Electron-deficient Olefins:

On the basis of above results, a plausible mechanism is proposed in Figure 5. The sp^2 C–H bond of enamide **1** is first activated by the Pd(II) complex to form the six-membered palladcycle intermediate **2**. Next, coordination of the acrylate to Pd followed by migratory insertion gives intermediate **5**. The target molecule **6** is finally obtained after *β*-hydride elimination. The Pd(0) that was generated is then recycled back to Pd^{2+} by the oxidant.

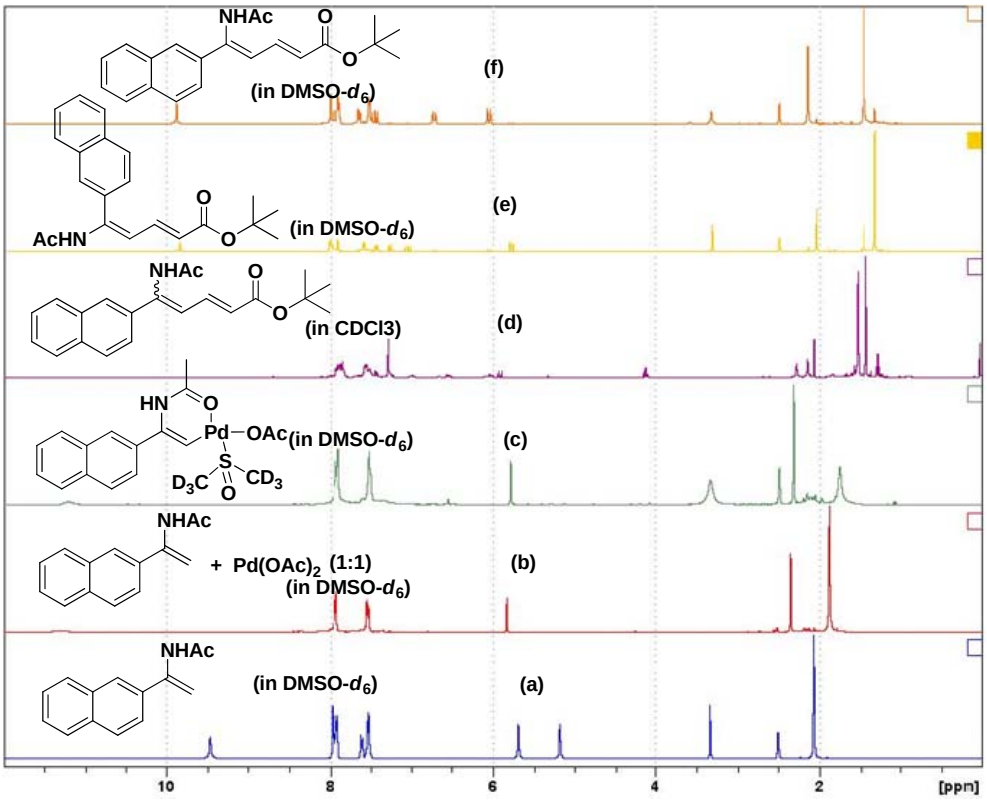


Figure 4. NMR investigation for the possible coupling intermediate complex

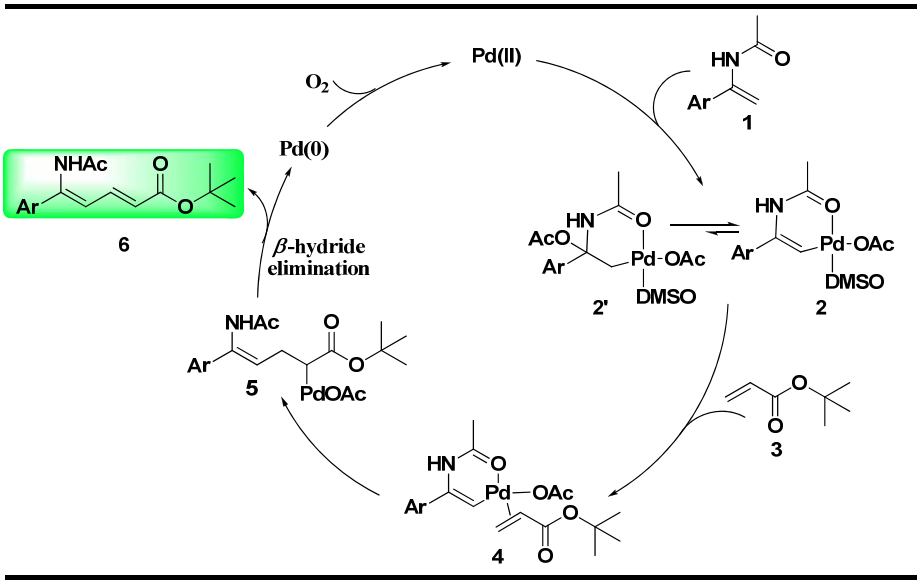
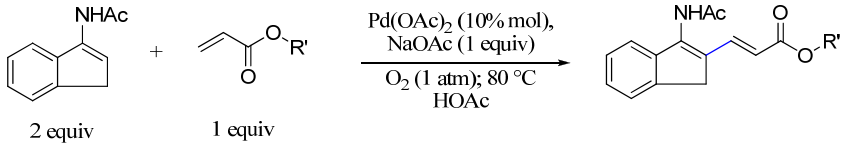


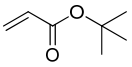
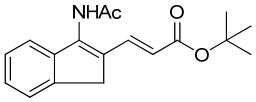
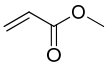
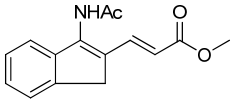
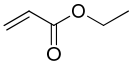
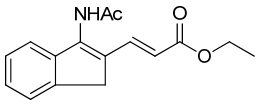
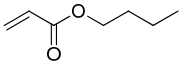
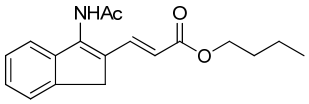
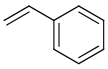
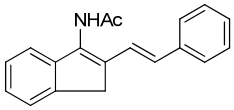
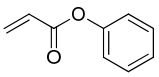
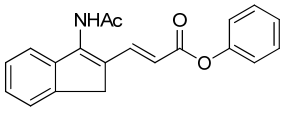
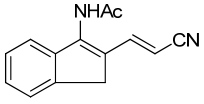
Figure 5. Proposed catalytic cycle for direct cross-coupling reaction of olefins

Representative Experimental Procedures for Direct Cross-Coupling Reaction:

A 5 mL dry round bottom flask was charged sequentially with a stirring bar, $Pd(OAc)_2$ (10 mol%, 0.02 mmol), NaOAc (1 equiv, 0.2 mmol), HOAc (0.5 ml) or DMSO as solvent. Then the flask was vacuumed and refilled with oxygen. The starting material enamide **1** (2 equiv, 0.4 mmol) and *tert*-butyl acrylate (1 equiv, 0.2 mmol) were added into the solution in sequence. The reaction mixture was stirred at 80 ºC under 1 atm of oxygen (balloon pressure) for 24 h. After cooling down, the mixture was diluted with ethyl acetate, filtered and washed with distilled water and brine. The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated to give the crude product which was purified on silica gel (EtOAc/Hexanes mixture).

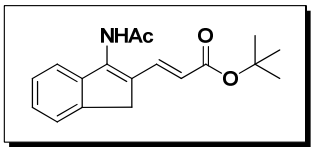
Table 1. Cross-coupling Reaction of *N*-(1H-inden-3-yl)acetamide with Different Coupling Partners.[a]



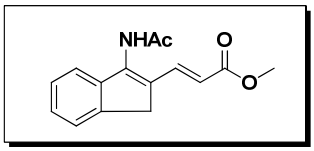
entry[a]	coupling partner	product	yield(%)[b] (E:Z)[c]
1			80 (>99:1)
2			72 (>99:1)
3			70 (>99:1)
4			74 (>99:1)
5			55 (>99:1)
6			68 (>99:1)
7			12 (>99:1)

(a) All the reaction were carried out at 80 °C for 24 h using *N*-(1*H*-inden-3-yl)acetamide (0.4 mmol, 2 equiv), acrylate (0.2 mmol, 1 equiv), $Pd(OAc)_2$ (0.02 mmol, 10 mol%), NaOAc (0.2 mmol, 1 equiv) and acetic acid (1.0 ml) under 1 atm oxygen atmosphere. (b) Isolated yield. (c) Determined by ^1H crude NMR.

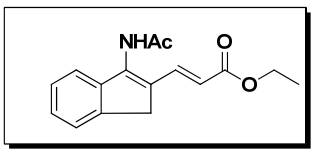
Characterization Datas:



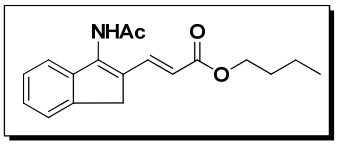
3a (*E*)-*tert*-butyl 3-(3-acetamido-1*H*-inden-2-yl)acrylate. m.p= 201-202 °C. R*f* = 0.35 (EA/Hexane=2:3). This compound was prepared by the general procedure described above and was obtained as a white solide. Yield = 80%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.02 (s, 1H), 7.61 (d, *J* = 15.6 Hz, 1H), 7.25-7.43 (m, 4H), 5.96 (d, *J* = 15.6 Hz, 1H), 3.60 (s, 2H), 2.14 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.1, 166.4, 142.3, 141.7, 141.5, 137.0, 130.3, 127.3, 126.6, 124.3, 121.8, 118.8, 80.1, 35.4, 28.3, 23.4. FTIR (NaCl, cm^{-1}): 3412, 2725, 1697, 1656, 1606, 1571, 1290, 1155. HRMS (ESI) *m/z* calculated for $C_{18}H_{21}NO_3Na$ $[M+Na]^+$: 322.1419, found 322.1424.



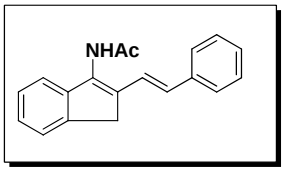
(*E*)-methyl 3-(3-acetamido-1*H*-inden-2-yl)acrylate. m.p = 226-228 °C. R*f* = 0.33 (EA/Hexane = 2:3).This compound was prepared by the general procedure described above and was obtained as a colorless oil. Yield = 72%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.10 (s, 1H), 7.69 (d, *J* = 16.0 Hz, 1H), 7.26-7.43 (m 4H), 6.04 (d, *J* = 16.0 Hz, 1H), 3.68 (s, 3H), 3.61 (s, 2H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.1, 166.8, 141.8, 141.6, 140.9, 137.3, 129.4, 126.9, 126.1, 123.8, 121.4, 116.1, 51.2, 34.9, 22.9. FTIR (NaCl, cm^{-1}): 3259, 1712, 1666, 1606, 1533, 1300, 1269, 1163, 1153. HRMS (ESI) *m/z* calculated for $C_{15}H_{15}NO_3Na$ $[M+Na]^+$: 280.0950, found 280.0941.



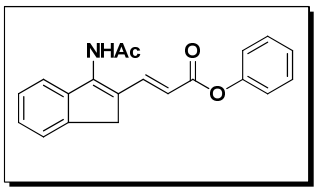
(*E*)-ethyl 3-(3-acetamido-1H-inden-2-yl)acrylate. m.p = 190-192 °C. R*f* = 0.33 (EA/Hexane = 2:3). This compound was prepared by the general procedure described above and was obtained as a colorless oil. Yield = 70%.^{1}H NMR (400 MHz, DMSO-d_6) 10.07 (s, 1H), 7.66 (d, *J* = 15.6 Hz, 1H), 7.27-7.42 (m, 4H), 6.03 (d, *J* = 15.6 Hz, 1H), 4.14 (q, *J* = 6.8 Hz, 2H), 3.81 (s, 2H), 2.13 (s, 3H), 1.21 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.3, 167.0, 142.3, 142.0, 141.4, 137.7, 130.3, 127.5, 126.7, 124.4, 121.8, 117.2, 60.3, 35.5, 23.4, 14.7. FTIR (NaCl, cm^{-1}): 1712, 1697, 1604, 1568, 1519, 1435, 1373, 1294, 1271. HRMS (ESI) m/z calculated for $C_{16}H_{17}NO_3Na$ $[M+Na]^+$: 294.1106, found 294.1105.



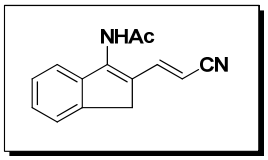
(*E*)-butyl 3-(3-acetamido-1*H*-inden-2-yl)acrylate. m.p = 178-180 °C. R*f* = 0.35 (EA/Hexane = 2:3). This compound was prepared by the general procedure described above and was obtained as a colorless oil. Yield = 74%. ^{1}H NMR (400 MHz, DMSO-d_6) 10.06 (s, 1H), 7.69 (d, *J* = 15.6 Hz, 1H), 7.26-7.44 (m, 4H), 6.04 (d, *J* = 15.6, 1H), 4.11 (t, *J* = 6.6 Hz, 2H), 3.62 (s, 2H), 2.14 (s, 3H), 1.56-1.62 (m, 2H), 1.31-1.40 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.1, 167.0, 142.4, 142.1, 141.5, 137.8, 130.1, 127.5, 126.7, 124.3, 121.9, 117.0, 63.9, 35.5, 30.8, 23.5, 19.1, 14.1. FTIR (NaCl, cm^{-1}): 1712, 1606, 1525, 1284, 1215, 1166. HRMS (ESI) m/z calculated for $C_{18}H_{21}NO_3Na$ $[M+Na]^+$: 322.1419, found 322.1406.



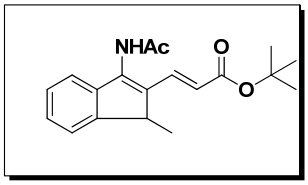
(*E*)-*N*-(2-styryl-1H-inden-3-yl)acetamide m.p = 227-229 °C. R*f* = 0.37 (EA/Hexane = 2:3). This compound was prepared by the General Procedure described above and was obtained as a colorless oil. Yield = 55%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.78 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.38-7.43 (m, 3H), 7.18-7.36 (m, 5H), 6.81 (d, *J* = 16.0 Hz, 1H), 3.68 (s, 2H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.0, 142.6, 141.4, 137.8, 136.4, 133.6, 129.2, 128.9, 127.9, 126.7, 126.5, 125.8, 124.0, 122.7, 120.8, 35.6, 23.5. FTIR (NaCl, cm^{-1}): 3256, 1645, 1507, 1374. HRMS (ESI) *m/z* calculated for $C_{19}H_{17}NONa$ $[M+Na]^+$: 298.1208, found 298.1206.



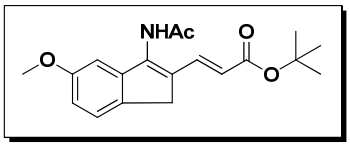
(*E*)-phenyl 3-(3-acetamido-1*H*-inden-2-yl)acrylate m.p = 214-215 °C. R*f* = 0.35 (EA/Hexane = 2:3). This compound was prepared by the General Procedure described above and was obtained as a colorless oil. Yield = 68%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.15 (s, 1H), 7.90 (d, *J* = 12.4 Hz, 1H), 7.42-7.46 (m, 4H), 7.25-7.28 (m, 3H), 7.16 (d, *J* = 6.2 Hz, 2H), 6.27 (d, *J* = 12.4 Hz, 1H), 3.71 (s, 2H), 2.15 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.2, 165.7, 151.1, 143.1, 142.7, 141.3, 139.8, 130.0, 127.8, 126.7, 126.2, 124.4, 122.3, 122.2, 115.8, 35.5, 23.5. FTIR (NaCl, cm^{-1}): 3249, 1733, 1670, 1615, 1530, 1527, 1423, 1286, 1138. HRMS (ESI) *m/z* calculated for $C_{20}H_{17}NO_3Na$ $[M+Na]^+$: 342.1106, found 342.1109.



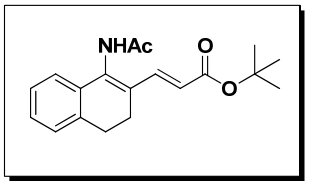
(*E*)-*N*-(2-(2-cyanovinyl)-1*H*-inden-3-yl)acetamide R*f* = 0.30 (EA/Hexane = 2:3). This compound was prepared by the General Procedure described above and was obtained as a colorless oil. Yield = 12%. ^{1}H NMR (300 MHz, Acetone-d_6) δ 9.23 (s, 1H), 7.64 (d, *J* = 16.2 Hz, 1H), 7.44-7.52 (m, 2H), 7.26-7.33 (m, 2H), 5.66 (d, *J* = 16.2 Hz, 1H), 3.63 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 173.5, 148.6, 147.3, 146.5, 146.2, 132.7, 131.6, 129.1, 126.4, 124.1, 96.8, 39.8, 27.8, 4.3. FTIR (NaCl, cm^{-1}): 3416, 2400, 2208, 1660. HRMS (ESI) *m/z* calculated for $C_{14}H_{12}N_2ONa$ $[M+Na]^+$: 247.0847, found 247.0853.



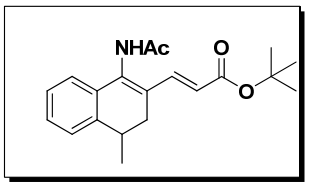
3b (*E*)-*tert*-butyl 3-(3-acetamido-1-methyl-1*H*-inden-2-yl)acrylate R*f* = 0.35 (EA/Hexane = 1:1). This compound was prepared by the General Procedure described above and was obtained as a colorless oil. Yield = 67%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.01 (s, 1H), 7.56 (d, *J* = 15.9 Hz, 1H), 7.45 (d, *J* =7.2 Hz, 1H), 7.32 (d, *J* = 6.8 Hz, 1H), 7.24-7.29 (m, 2H), 5.86 (d, *J* = 15.9 Hz, 1H), 3.69, (q, *J* =7.2 Hz, 1H), 2.14 (s, 3H), 1.46 (s, 9H), 1.25 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.1, 166.4, 149.3, 141.2, 139.8, 136.0, 135.1, 127.6, 126.8, 123.4, 122.0, 119.3, 80.1, 28.3, 23.4, 18.6. FTIR (NaCl, cm^{-1}): 3402, 1695, 1653, 1603, 1570, 1292, 1152. HRMS (ESI) *m/z* calculated for $C_{19}H_{23}NO_3Na$ $[M+Na]^+$: 336.1576, found 336.1568.



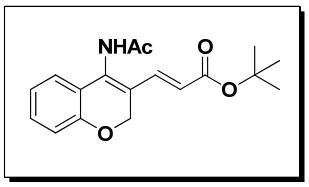
3c (*E*)-*tert*-butyl 3-(3-acetamido-5-methoxy-1*H*-inden-2-yl)acrylate. m.p = 200-201 °C. R*f* = 0.33 (EA/Hexane = 1:1). This compound was prepared by the general procedure described above and was obtained as a colorless oil. Yield = 79%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.97 (s, 1H), 7.56 (d, *J* = 15.6 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 6.82-6.91 (m, 2H), 5.92 (d, *J* = 15.6 Hz, 1H), 3.73 (s, 3H), 3.51 (s, 2H), 2.13 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 166.4, 158.8, 142.9, 141.4, 137.2, 134.4, 131.6, 124.9, 118.7, 113.8, 106.7, 80.1, 55.7, 34.7, 28.3, 23.5. FTIR (NaCl, cm^{-1}): 2968, 1660, 1608, 1300, 1143. HRMS (ESI) m/z calculated for $C_{19}H_{23}NO_4Na$ $[M+Na]^+$: 352.1525, found 352.1516.



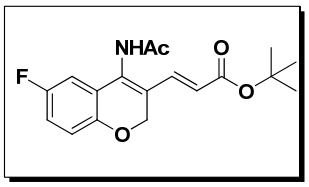
3d (*E*)-*tert*-butyl 3-(1-acetamido-3,4-dihydronaphthalen-2-yl)acrylate. m.p = 169-171 °C. R*f* = 0.35 (EA/Hexane = 3:2).This compound was prepared by the general procedure described above and was obtained as a colorless oil. Yield = 74%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.51 (s, 1H), 7.58 (d, *J* = 15.5 Hz, 1H), 7.19-7.21 (m, 4H), 5.98 (d, *J* = 15.5 Hz, 1H), 2.76 (t, *J* = 7.8 Hz, 2H), 2.48 (t, *J* = 7.8 Hz, 2H), 2.09 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.4, 166.4, 140.7, 137.4, 136.6, 132.7, 128.9, 128.8, 127.8, 126.8, 124.7, 119.7, 80.1, 28.3, 27.1, 23.1, 23.0. FTIR (NaCl, cm^{-1}): 1666, 1612, 1504, 1369, 1311, 1151. HRMS (ESI) m/z calculated for $C_{19}H_{23}O_3NNa$ $[M+Na]^+$: 336.1576, found 336.1578.



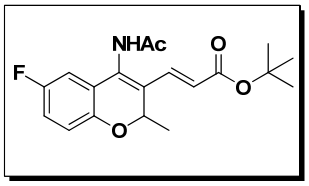
3e (*E*)-*tert*-butyl 3-(1-acetamido-4-methyl-3,4-dihydronaphthalen-2-yl)acrylate m.p = 180-183 °C. R*f* = 0.33 (EA/Hexane = 3:2). This compound was prepared by the General Procedure described above and was obtained as a colorless oil. Yield = 57%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.51(s, 1H), 7.58 (d, *J* = 15.6 Hz, 1H), 7.21-7.25 (m, 4H), 5.98 (d, *J*= 15.6 Hz, 1H), 2.93 (m, 1H), 2.59 (dd, *J* = 16.0, 6.0Hz, 1H), 2.33 (dd, *J* = 16.0, 6.4Hz, 1H), 2.08 (s, 3H), 1.44 (s, 9H), 1.15 (d, *J* =6.8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.6, 166.5, 142.4, 141.0, 135.9, 131.9, 129.2, 127.3, 126.7, 126.5, 124.6, 119.7, 80.2, 31.3, 30.5, 28.2, 23.0, 20.2. FTIR (NaCl, cm^{-1}): 3422, 1704, 1654, 1617, 1312, 1274, 1155. HRMS (ESI) *m/z* calculated for $C_{20}H_{25}NO_3Na$ $[M+Na]^+$: 350.1732, found 350.1726.



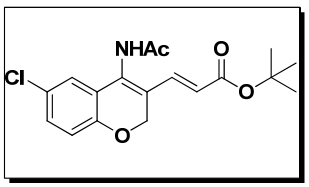
3f (*E*)-*tert*-butyl 3-(4-acetamido-2*H*-chromen-3-yl)acrylate. R*f* = 0.33 (EA/Hexane = 3:2). This compound was prepared by the General Procedure described above and was obtained as a colorless oil. Yield = 76%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.60 (s, 1H), 7.37 (d, *J* = 16.0 Hz, 2H), 7.16-7.23 (m, 2H), 6.85-6.95 (m, 2H), 5.91 (d, *J* = 16.0 Hz, 1H), 4.96 (s, 2H), 2.09 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.5, 166.1, 155.6, 136.7, 133.6, 131.2, 125.3, 122.1, 121.9, 121.5, 119.9, 116.3, 80.4, 65.1, 28.2, 23.1. FTIR (NaCl, cm^{-1}): 1699, 1598, 1514, 1485.19, 1367, 1321, 1273, 1151. HRMS (ESI) m/z calculated for $C_{18}H_{21}O_4NNa$ $[M+Na]^+$: 338.1368, found 338.1370.



3g (*E*)-*tert*-butyl 3-(4-acetamido-6-fluoro-2*H*-chromen-3-yl)acrylate Mp = 162-164 °C. R*f* = 0.30 (EA/Hexane = 3:2). This compound was prepared by the General Procedure described above and was obtained as a colorless oil. Yield = 55%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.67 (s, 1H), 7.37 (d, *J* = 16.0 Hz, 1H), 6.90-7.10 (m, 3H), 5.99 (d, *J* = 16.0 Hz, 1H), 4.99 (s, 1H), 2.13 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.7, 166.0, 157.3 (*J*= 235.0 Hz), 151.7, 136.4, 132.8, 123.3, 122.9 (*J* = 8.0 Hz), 120.8, 117.7 (*J* = 9.0 Hz), 117.4 (*J* = 24.0 Hz), 111.5 (*J* = 25.0 Hz), 80.5, 65.3, 28.2, 23.2. FTIR (NaCl, cm^{-1}): 3415, 1700, 1662, 1625, 1301, 1151. HRMS (ESI) *m/z* calculated for $C_{18}H_{20}NO_4FNa$ $[M+Na]^+$: 356.1274, found 356.1275.

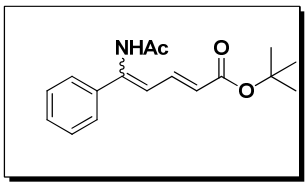


3h (*E*)-*tert*-butyl 3-(4-acetamido-6-fluoro-2-methyl-2*H*-chromen-3-yl)acrylate m.p = 153-156 °C. R*f* = 0.32 (EA/Hexane = 3:2). This compound was prepared by the General Procedure described above and was obtained as a colorless oil. Yield = 57%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.64 (s, 1H), 7.38 (d, *J* = 16.0 Hz, 1H), 7.07-7.12 (m, 1H), 6.99-7.03 (m, 1H), 6.89-6.93 (m, 1H), 6.02 (d, *J* = 16.0 Hz, 1H), 5.46 (q, *J* = 6.4 Hz, 1H), 2.12 (s, 3H), 1.44 (s, 9H), 1.23 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.6, 166.0, 157.2 (*J*=235.0 Hz), 149.2, 136.6, 131.9, 127.7, 122.1 (*J* = 8.0 Hz), 120.2, 118.6 (*J* = 8.0 Hz), 117.7 (*J* = 24.0), 111.3 (*J* = 24.0 Hz), 80.5, 70.9, 28.2, 23.2, 19.0. FTIR (NaCl, cm^{-1}): 1705, 1664, 1300, 1287, 1161. HRMS (ESI) *m/z* calculated for $C_{19}H_{22}NO_4FNa$ $[M+Na]^+$: 370.1431, found 370.1429.

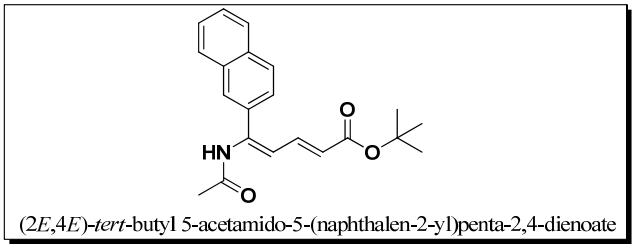


3i (*E*)-*tert*-butyl 3-(4-acetamido-6-chloro-2*H*-chromen-3-yl)acrylate m.p= 174-177 °C. R*f* = 0.31 (EA/Hexane = 3:2). This compound was prepared by the General Procedure described above and was obtained as a colorless oil. Yield = 65%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.68 (s, 1H), 7.37 (d, *J* = 16.0 Hz, 1H), 7.26 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.19 (d, *J* = 2.4 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 1H), 5.99 (d, *J* = 16.0 Hz, 1H), 5.03 (s, 2H), 2.14 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.7, 165.9, 154.2, 136.3,

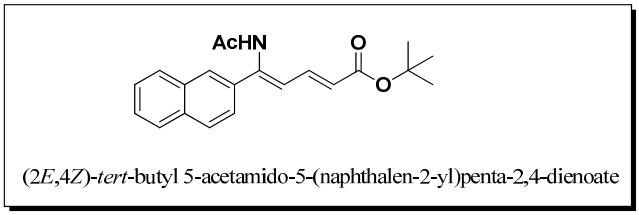
132.2, 130.5, 125.8, 124.5, 123.2, 123.1, 120.9, 118.2, 80.6, 65.4, 28.2, 23.2. FTIR (NaCl, cm^{-1}): 3271, 1701, 1665, 1617, 1302, 1152. HRMS (ESI) *m/z* calculated for $C_{18}H_{20}NO_4ClNa$ $[M+Na]^+$: 372.0979, found 372.0972.



3j *tert*-butyl 5-acetamido-5-phenylpenta-2,4-dienoate (E:Z = 60:40) R*f* = 0.35 (EA/Hexane = 2:3). This compound was prepared by the General Procedure described above and was obtained as a colorless oil. Yield = 67%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.75 (s, 0.85H), 9.70 (s, 0.72H), 7.45-7.48 (m, 4.3H), 7.20-7.41 (m, 6.5H), 6.94-7.03 (dd, *J* = 15.0, 15.0 Hz, 0.67H), 6.55 (d, *J* = 11.6 Hz, 1H), 5.99 (d, *J* = 15.5 Hz, 1H), 5.73 (d, *J* = 15.0 Hz, 0.68H), 2.06 (s, 3H), 2.00 (s, 2.1H), 1.43 (s, 9H), 1.34 (s, 1.3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 169.9, 169.1, 166.3, 166.2, 145.4, 142.7, 141.8, 140.0, 137.4, 135.5, 129.8, 129.5, 129.3, 128.8, 128.8, 126.6, 122.9, 119.4, 112.3, 80.1, 79.5, 28.2, 28.1, 24.5, 23.3. FTIR (NaCl, cm^{-1}): 3222, 1691, 1668, 1621, 1301, 1284, 1158. HRMS (ESI) *m/z* calculated for $C_{17}H_{21}NO_3Na$ $[M+Na]^+$: 310.1419, found 310.1415.



(2*E*,4*E*)-*tert*-butyl 5-acetamido-5-(naphthalen-2-yl)penta-2,4-dienoate

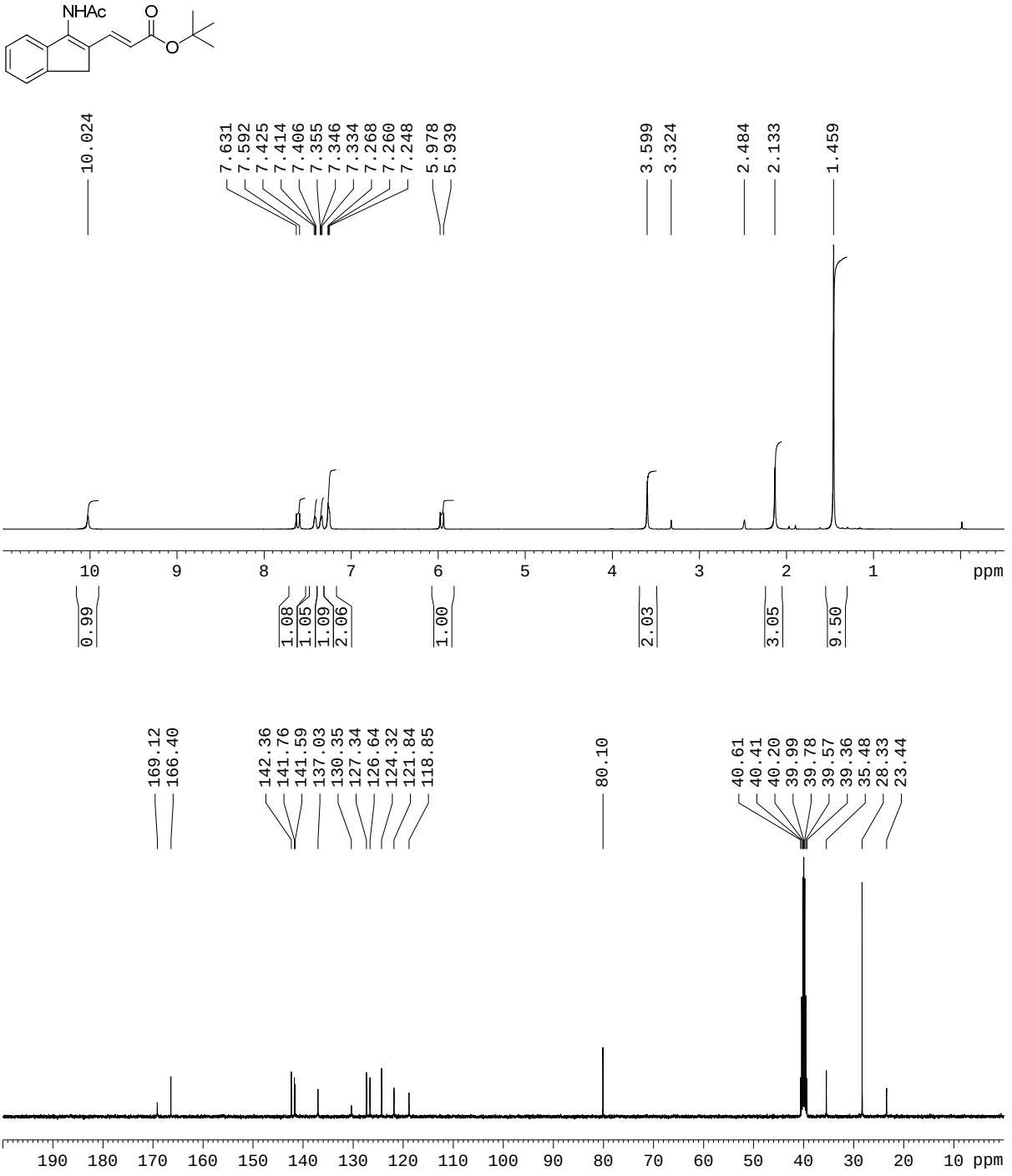


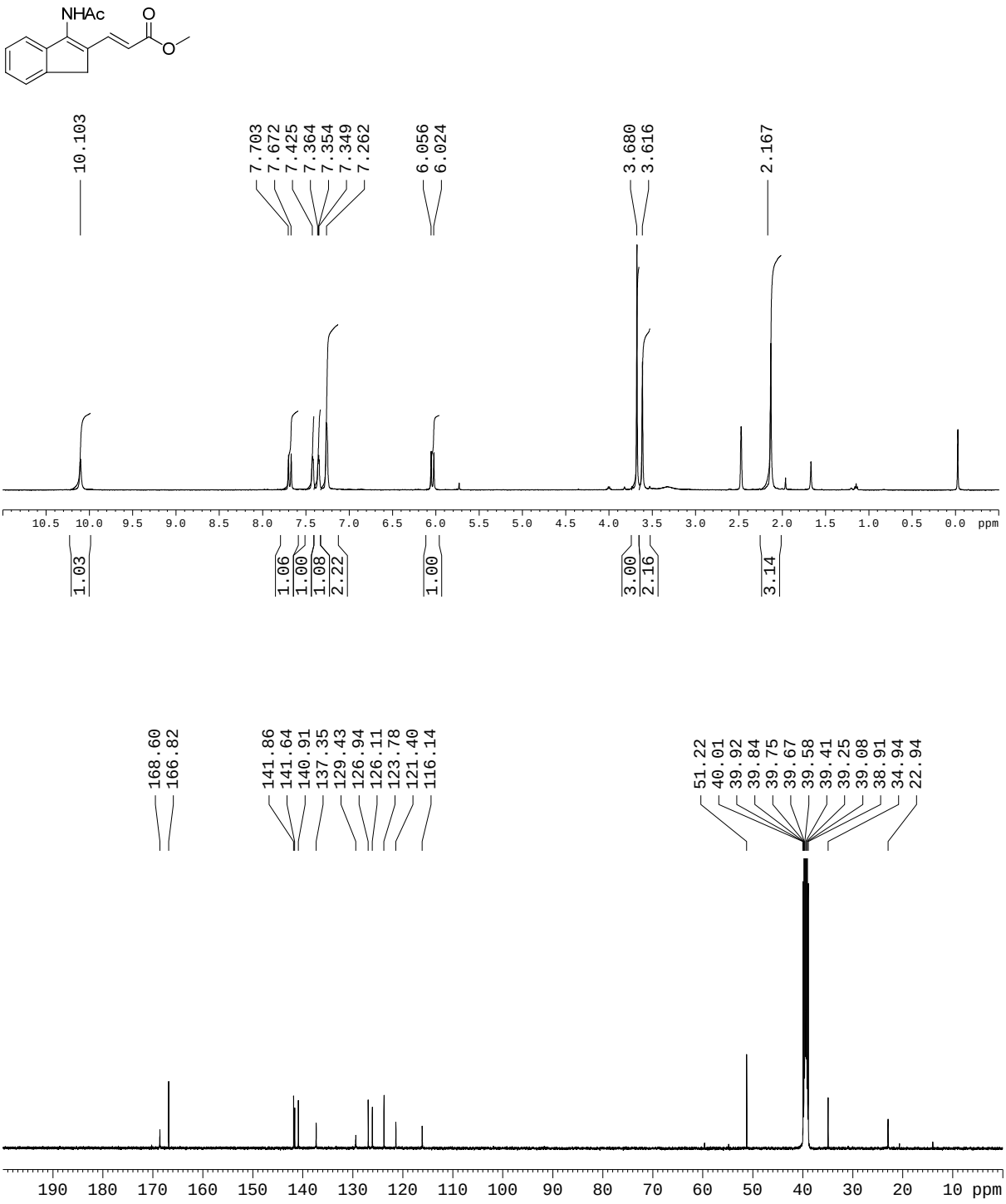
(2*E*,4*Z*)-*tert*-butyl 5-acetamido-5-(naphthalen-2-yl)penta-2,4-dienoate

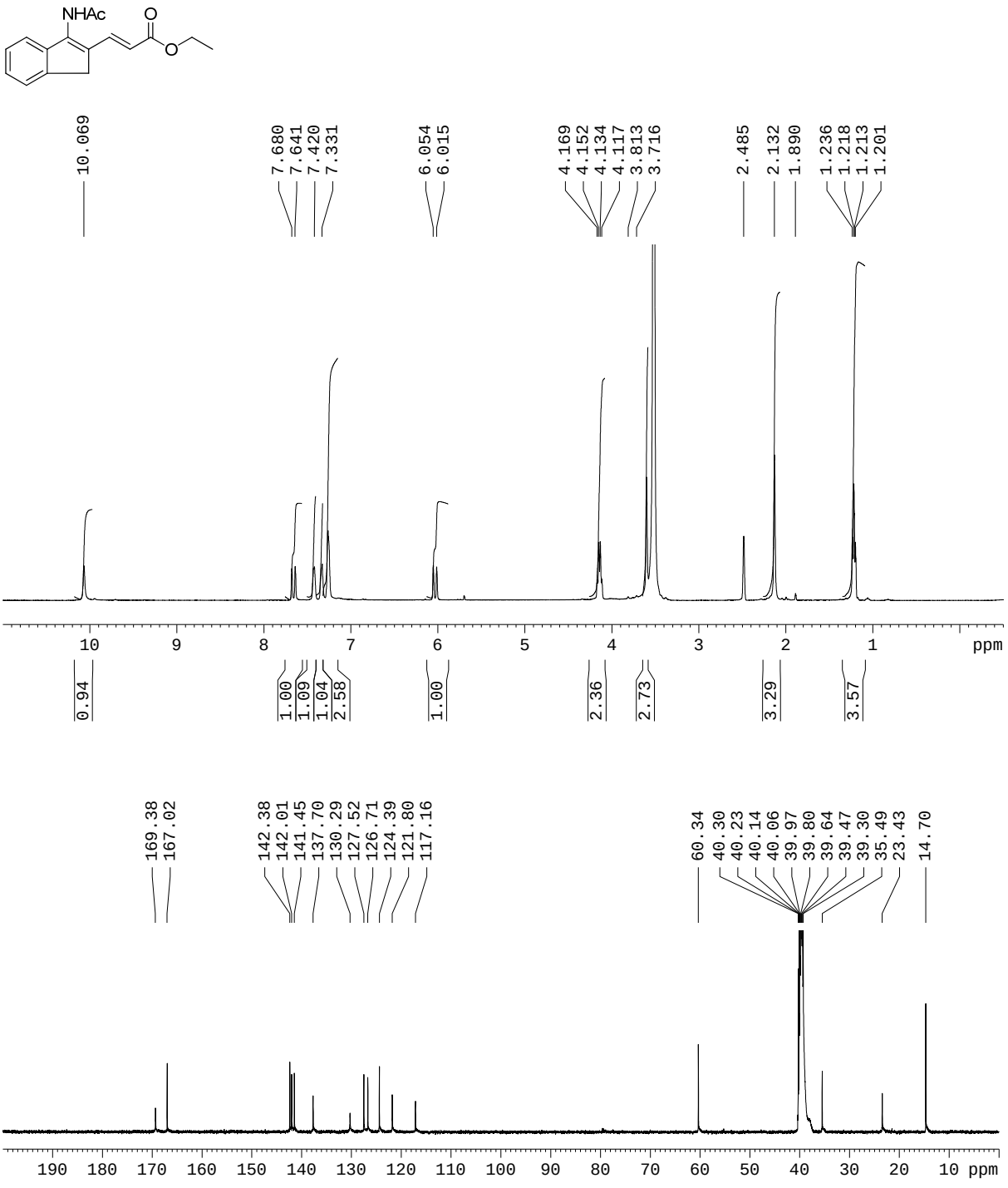
3k$_1$ (2*E*, 4*E*)-*tert*-butyl 5-acetamido-5-(naphthalene-2-yl)penta-2,4-dienoate T R*f* = 0.35 (EA/Hexane = 2:3). his compound was prepared by the General Procedure described above and was obtained as a colorless oil. Yield = 26%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.83 (s, 1H), 7.95-8.01 (m, 3H), 7.89 (s, 1H), 7.56-7.60 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 12.1 Hz, 1H), 7.01-7.08 (dd, *J* = 12.1 Hz, *J* = 14.9 Hz, 1H), 5.78 (d, *J* = 14.9 Hz, 1H), 2.03 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.9, 166.4, 145.4, 142.7, 133.4, 133.0, 132.9, 129.1, 128.7, 128.3, 128.1, 127.5, 127.3, 127.2, 119.6, 112.7, 79.6, 28.3, 24.6. FTIR (NaCl, cm^{-1}): 3053, 2981, 1693, 1614, 1504, 1367, 1265, 1138, 989, 894. HRMS (ESI) *m/z* calculated for $C_{21}H_{23}NO_3Na$ $[M+Na]^+$: 360.1576, found 360.1579.

3k$_2$ (2*E*, 4*Z*)-*tert*-butyl 5-acetamido-5-(naphthalene-2-yl)penta-2,4-dienoate R*f* = 0.33 (EA/Hexane = 2:3). This compound was prepared by the General Procedure described above and was obtained as a colorless oil. Yield = 38%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.88 (s, 1H), 7.99 (s, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.87-7.89

(m, 2H), 7.64 (d, J = 8.6 Hz, 1H), 7.50-7.52 (m, 2H), 7.41-7.47 (dd, J = 11.4 Hz, J = 15.1 Hz, 1H), 6.73 (d, J = 11.4, 1H), 6.05 (d, J = 15.1 Hz, 1H), 2.13 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.3, 166.3, 141.9, 140.1, 134.9, 133.6, 133.2, 128.9, 128.3, 127.9, 127.1, 126.9, 125.9, 124.4, 123.1, 120.1, 80.1, 28.3, 23.4. FTIR (NaCl, cm^{-1}): 3053, 2983, 1693, 1614, 1504, 1367, 1317, 1265, 1139, 985, 894. HRMS (ESI) *m/z* calculated for $C_{21}H_{23}NO_3Na$ $[M+Na]^+$: 360.1576, found 360.1579.



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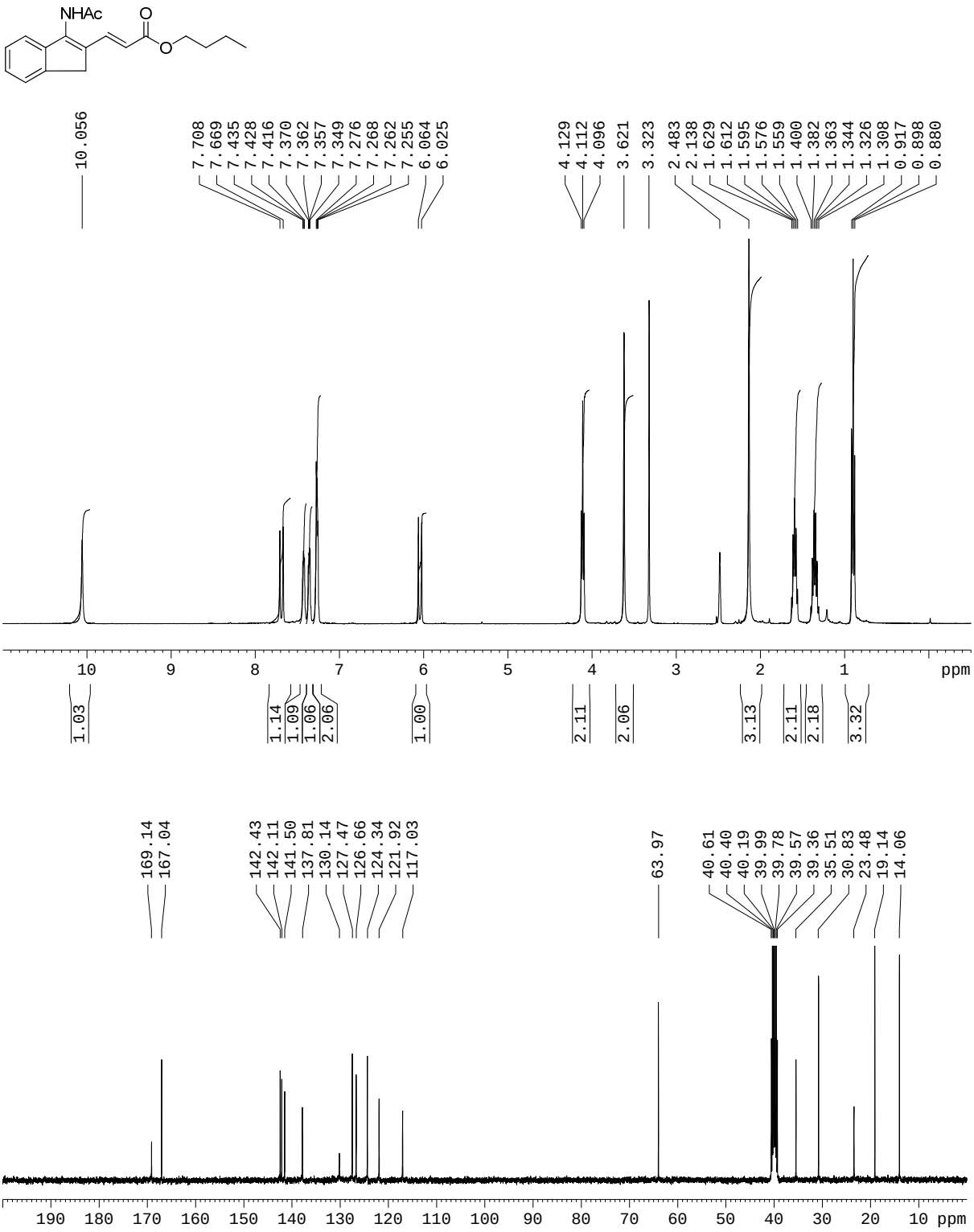
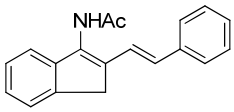
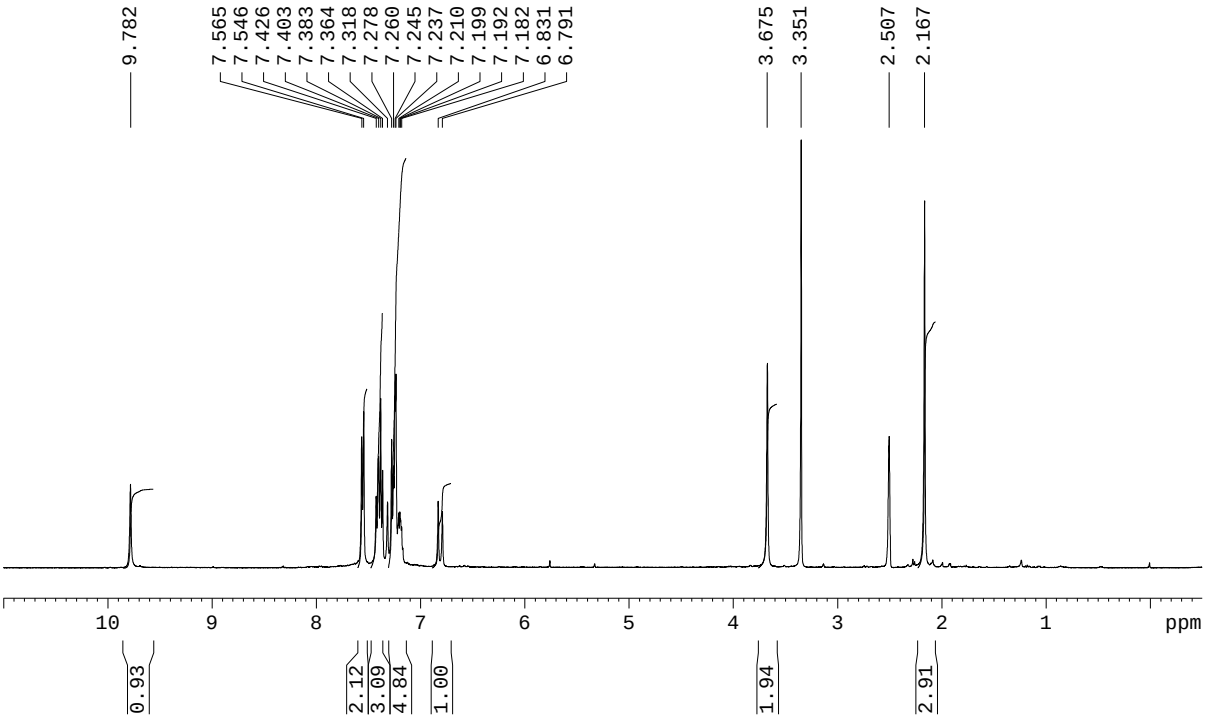



NHAc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7.546
7.426
7.403
7.383
7.364
7.318
7.278
7.260
7.245
7.237
7.210
7.199
7.192
7.182
6.831
6.791
3.675
3.351
2.507
2.167
10
9
8
7
6
5
4
3
2
1
ppm
0.93
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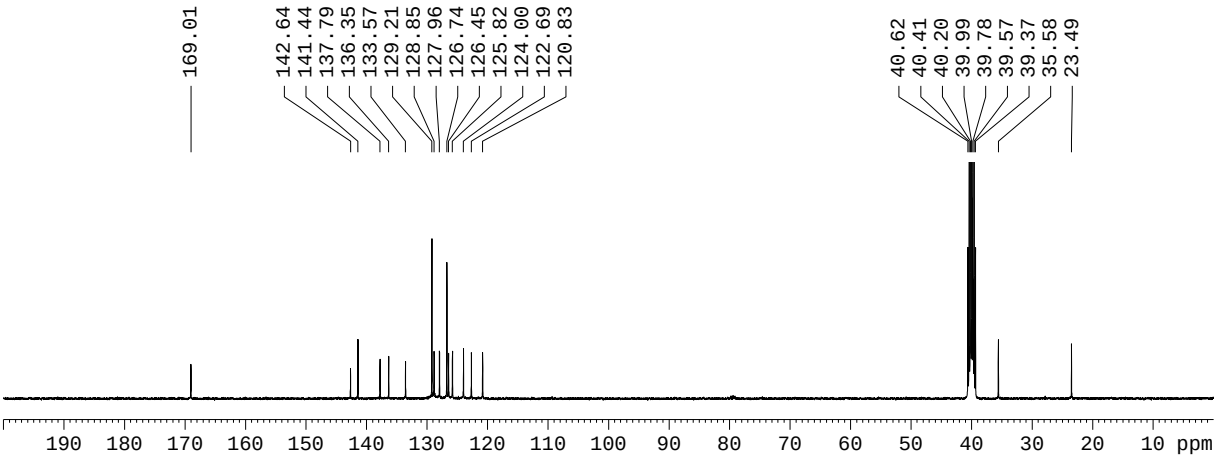
3.09
4.84
1.00
1.94
2.91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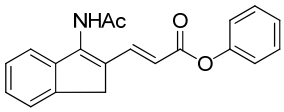
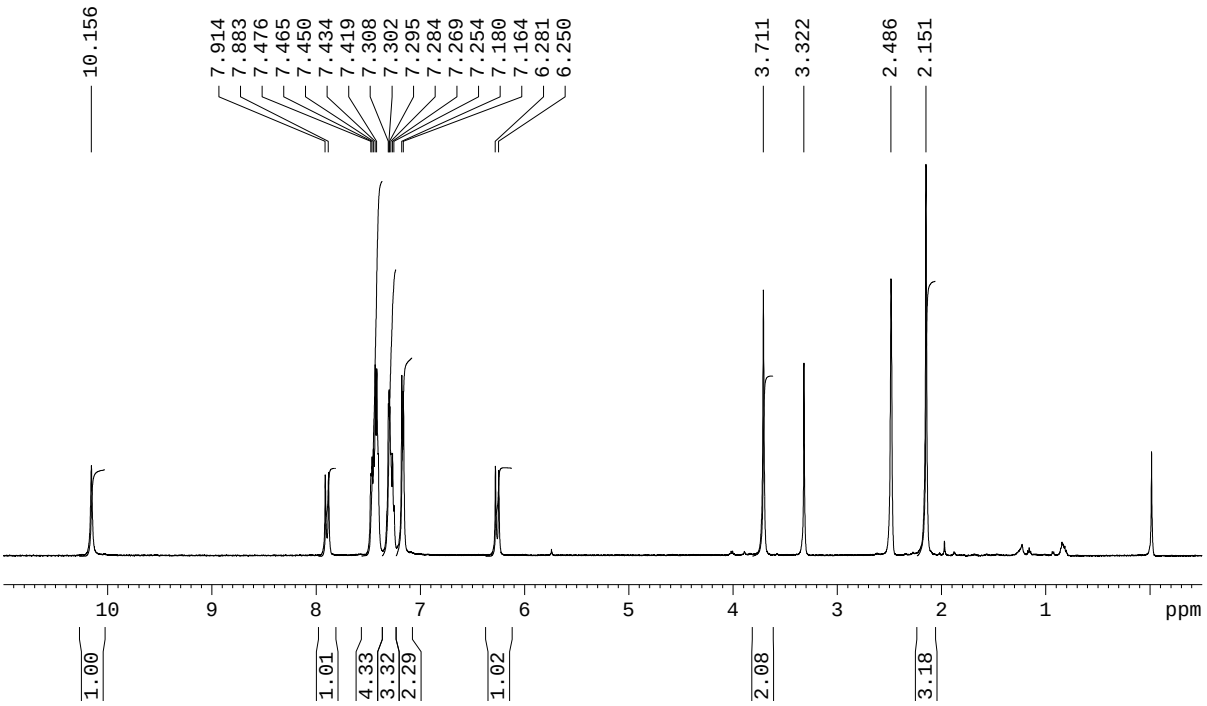
142.64
141.44
137.79
136.35
133.57
129.21
128.85
127.96
126.74
126.45
125.82
124.00
122.69
120.83
40.62
40.41
40.20
39.99
39.78
39.57
39.37
35.58
23.49
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


NHAc
O
O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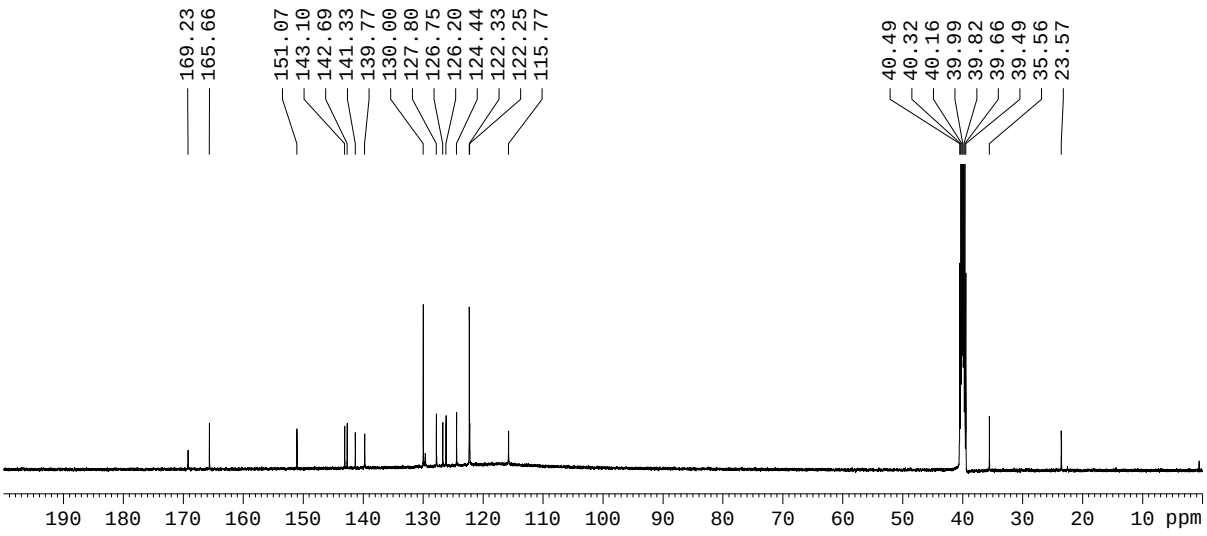
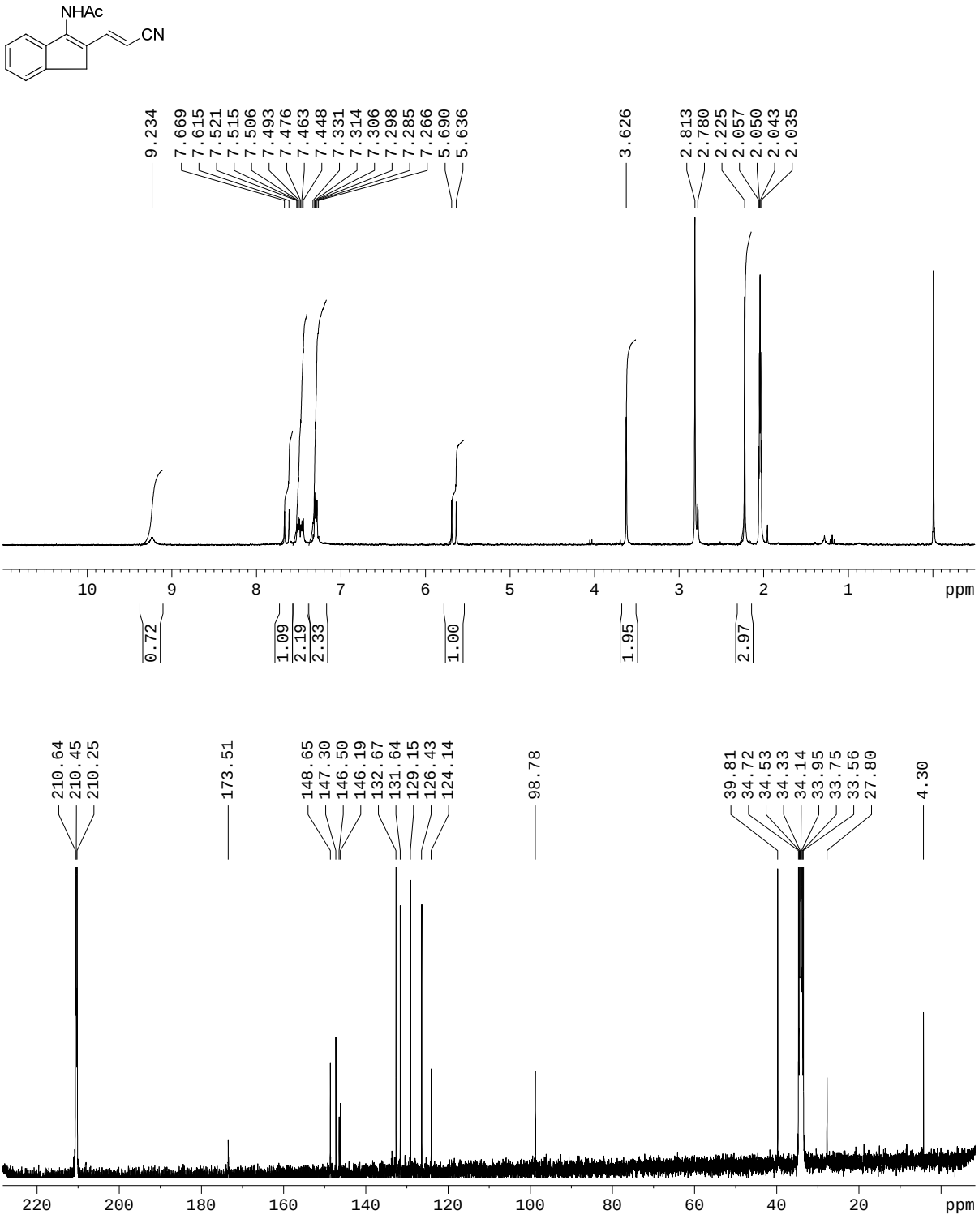
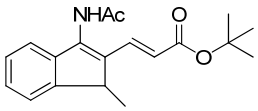
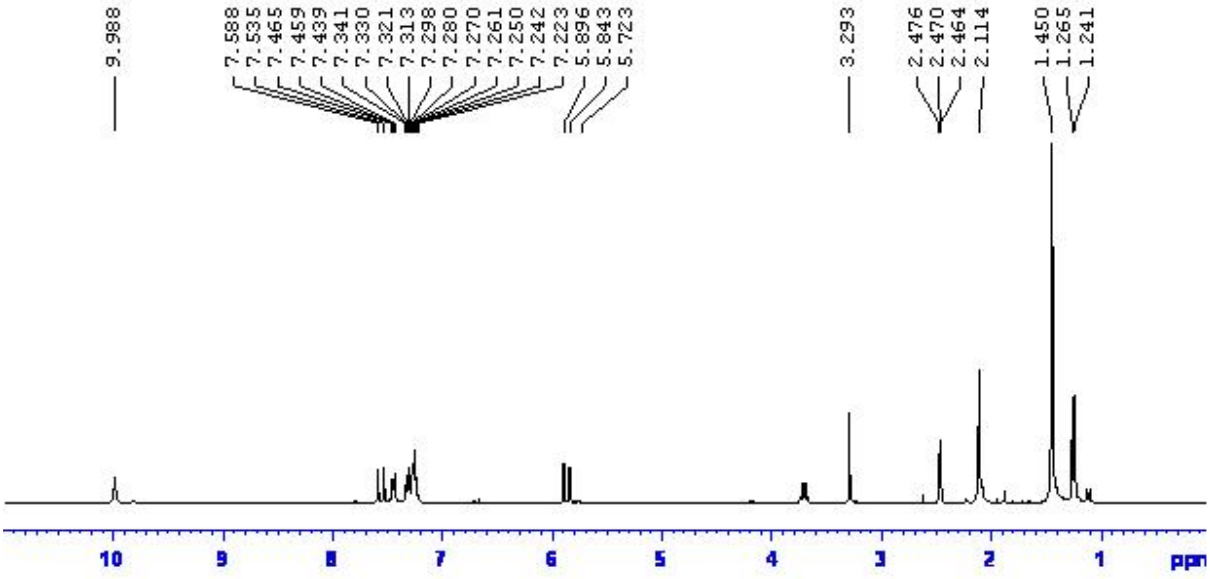
7.914
7.883
7.476
7.465
7.450
7.434
7.419
7.308
7.302
7.295
7.284
7.269
7.254
7.180
7.164
6.281
6.250
3.711
3.322
2.486
2.151
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
4.33
3.32
2.29
1.02
2.08
3.18


169.23
165.66
151.07
143.10
142.69
141.33
139.77
130.00
127.80
126.75
126.20
124.44
122.33
122.25
115.77
40.49
40.32
40.16
39.99
39.82
39.66
39.49
35.56
23.57
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm




NHAc
O
O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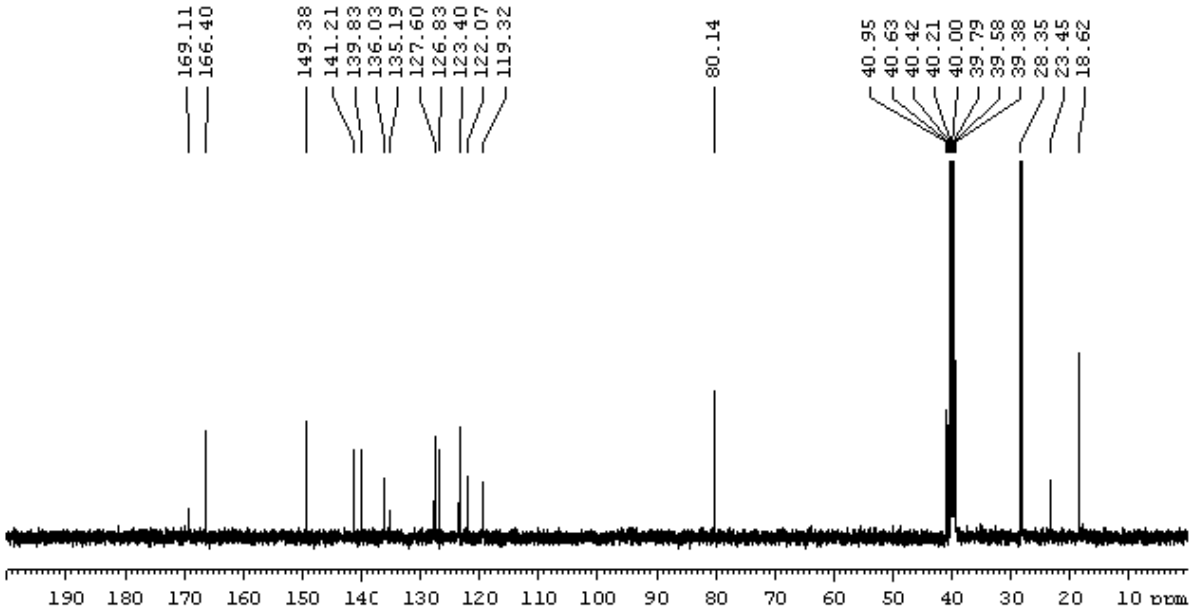
7.588
7.535
7.465
7.459
7.439
7.341
7.330
7.321
7.313
7.298
7.280
7.270
7.261
7.250
7.242
7.223
5.896
5.843
5.723
3.293
2.476
2.470
2.464
2.114
1.450
1.265
1.241
10
9
8
7
6
5
4
3
2
1
ppm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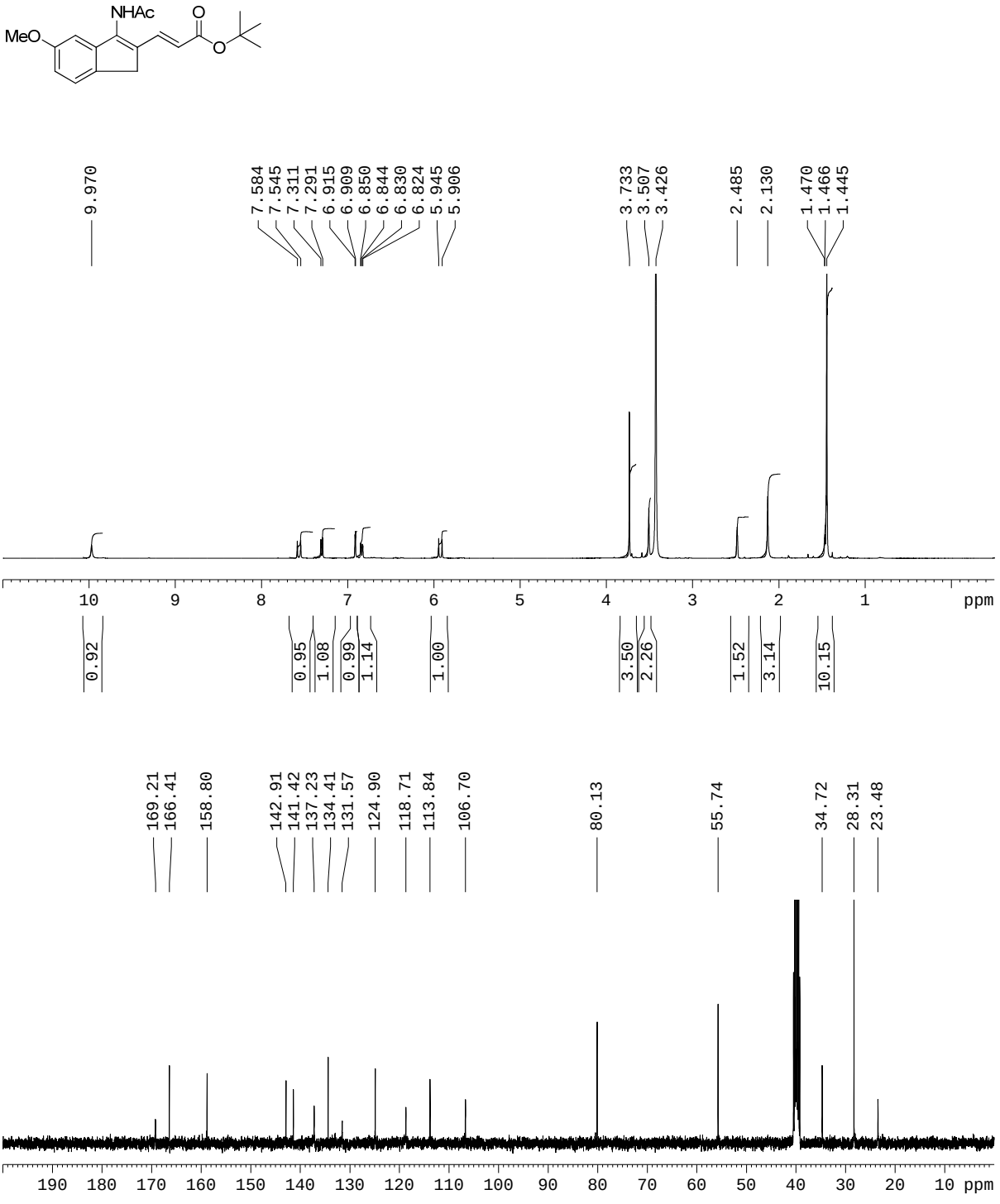
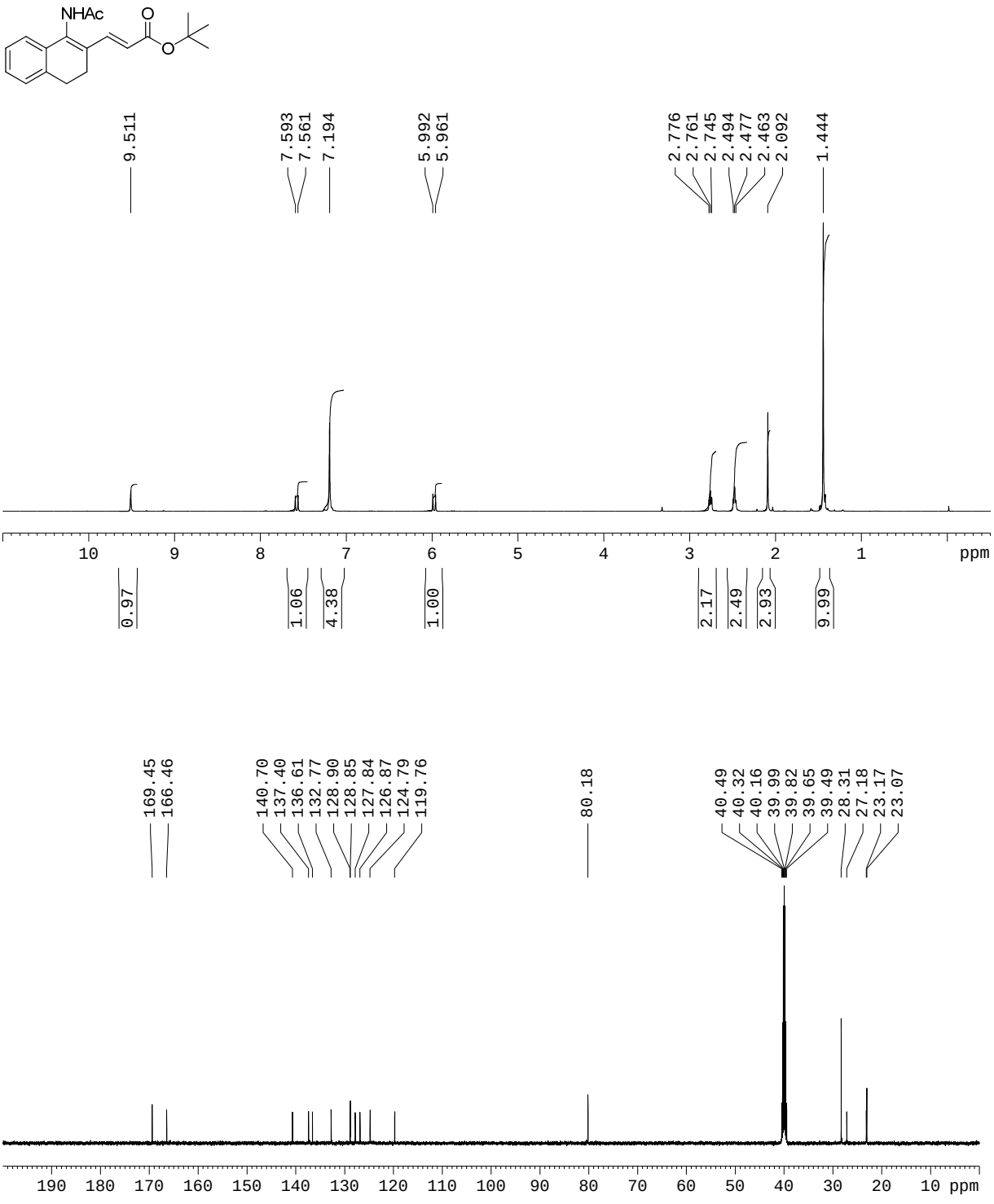
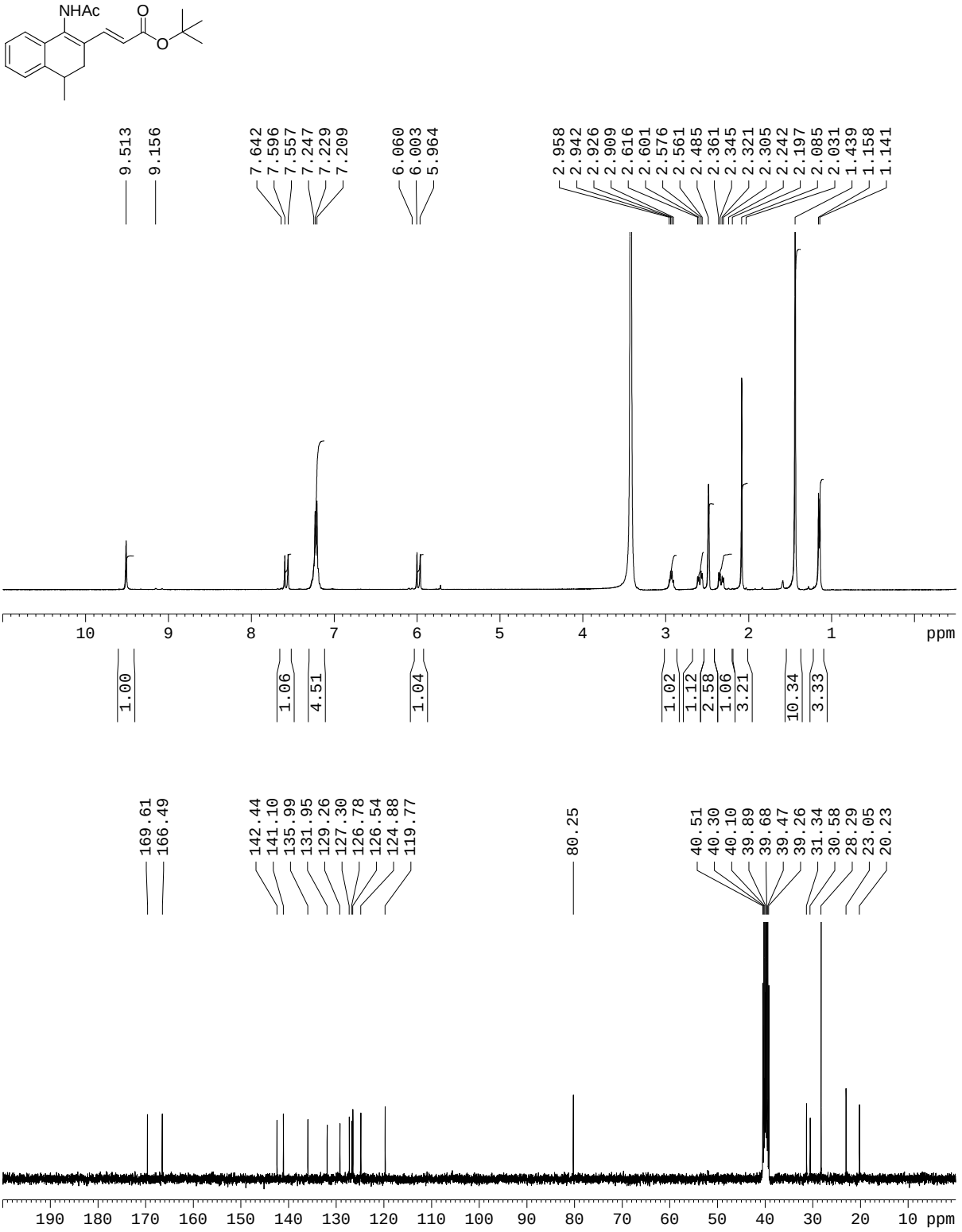
166.40
149.38
141.21
139.83
136.03
135.19
127.60
126.83
123.40
122.07
119.32
80.14
40.95
40.63
40.42
40.21
40.00
39.79
39.58
39.38
28.35
23.45
18.62
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


NHAc
O
MeO
O
9.970
7.584
7.545
7.311
7.291
6.915
6.909
6.850
6.844
6.830
6.824
5.945
5.906
3.733
3.507
3.426
2.485
2.130
1.470
1.466
1.445
10
9
8
7
6
5
4
3
2
1
ppm
0.92
0.95
1.08
0.99
1.14
1.00
3.50
2.26
1.52
3.14
10.15
169.21
166.41
158.80
142.91
141.42
137.23
134.41
131.57
124.90
118.71
113.84
106.70
80.13
55.74
34.72
28.31
23.48
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


NHAc
O
O
9.511
7.593
7.561
7.194
5.992
5.961
2.776
2.761
2.745
2.494
2.477
2.463
2.092
1.444
10
9
8
7
6
5
4
3
2
1
ppm
0.97
1.06
4.38
1.00
2.17
2.49
2.93
9.99
169.45
166.46
140.70
137.40
136.61
132.77
128.90
128.85
127.84
126.87
124.79
119.76
80.18
40.49
40.32
40.16
39.99
39.82
39.65
39.49
28.31
27.18
23.17
23.07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


NHAc
O
O
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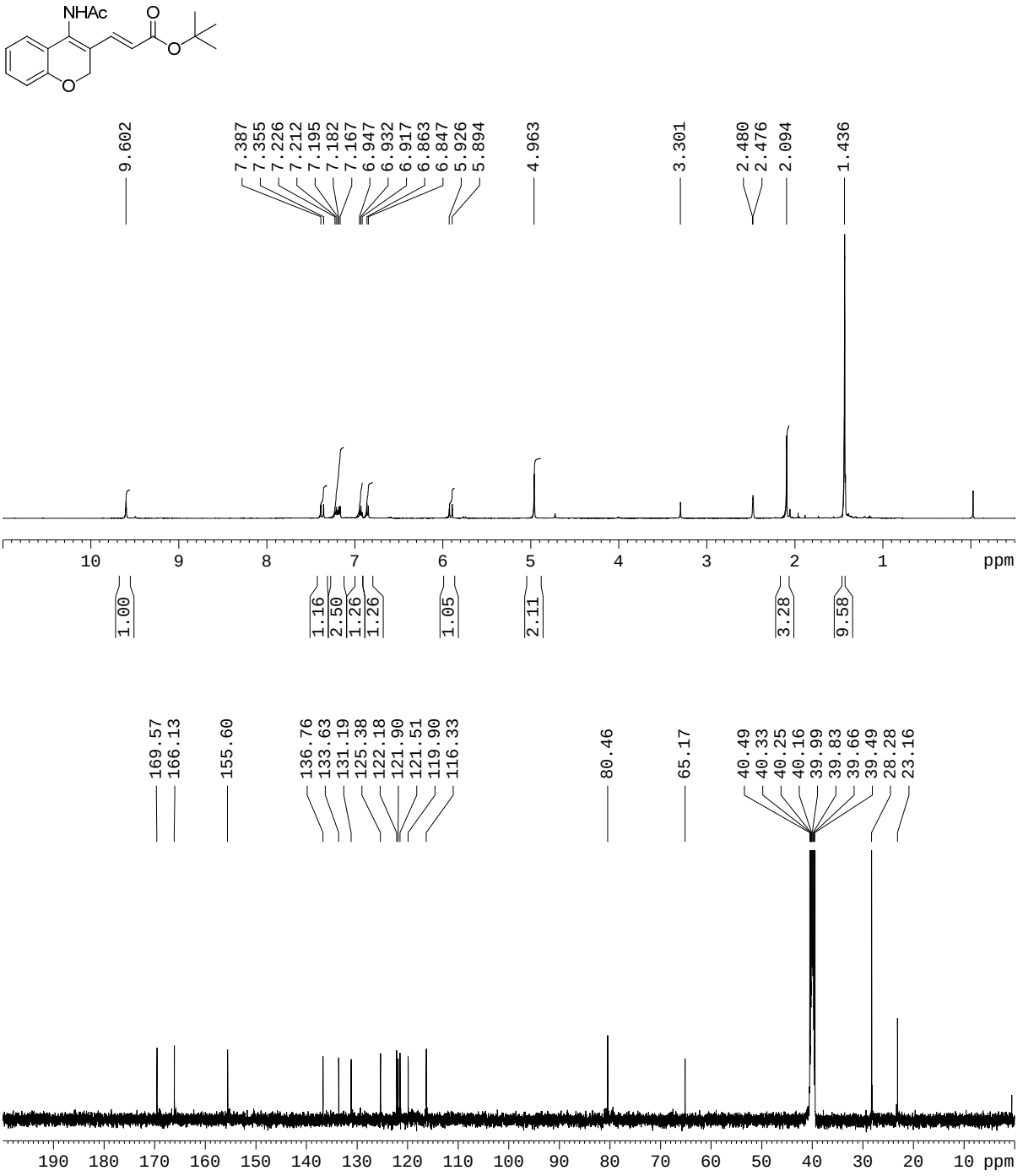
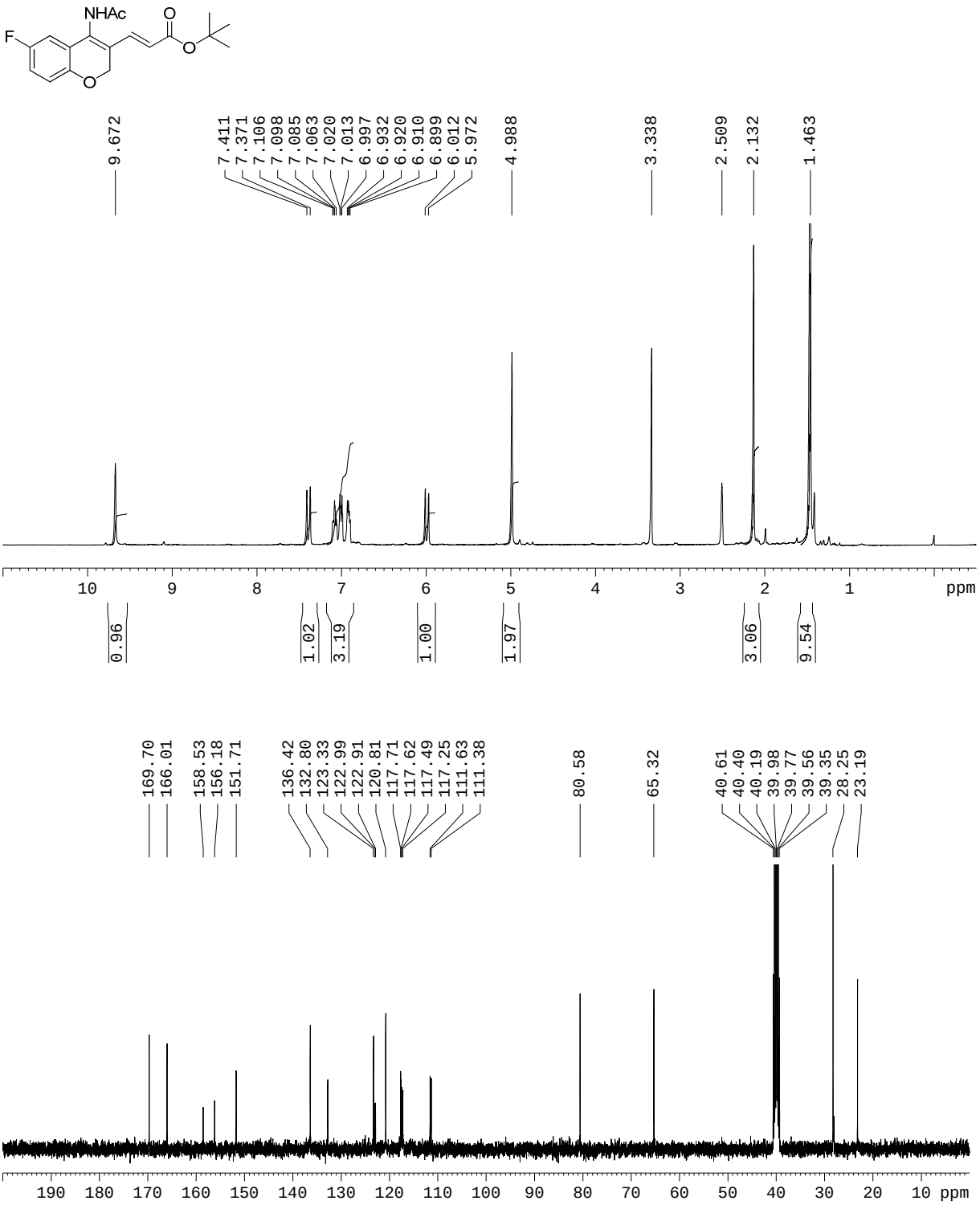
9.156
7.642
7.596
7.557
7.247
7.229
7.209
6.060
6.003
5.964
2.958
2.942
2.926
2.909
2.616
2.601
2.576
2.561
2.485
2.361
2.345
2.321
2.305
2.242
2.197
2.085
2.031
1.439
1.158
1.141
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.06
4.51
1.04
1.02
1.12
2.58
1.06
3.21
10.34
3.33
169.61
166.49
142.44
141.10
135.99
131.95
129.26
127.30
126.78
126.54
124.88
119.77
80.25
40.51
40.30
40.10
39.89
39.68
39.47
39.26
31.34
30.58
28.29
23.05
20.23
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


NHAc
O
O
O
9.602
7.387
7.355
7.226
7.212
7.195
7.182
7.167
6.947
6.932
6.917
6.863
6.847
5.926
5.894
4.963
3.301
2.480
2.476
2.094
1.436
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.16
2.50
1.26
1.26
1.05
2.11
3.28
9.58
169.57
166.13
155.60
136.76
133.63
131.19
125.38
122.18
121.90
121.51
119.90
116.33
80.46
65.17
40.49
40.33
40.25
40.16
39.99
39.83
39.66
39.49
28.28
23.16
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


NHAc
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F
O
O
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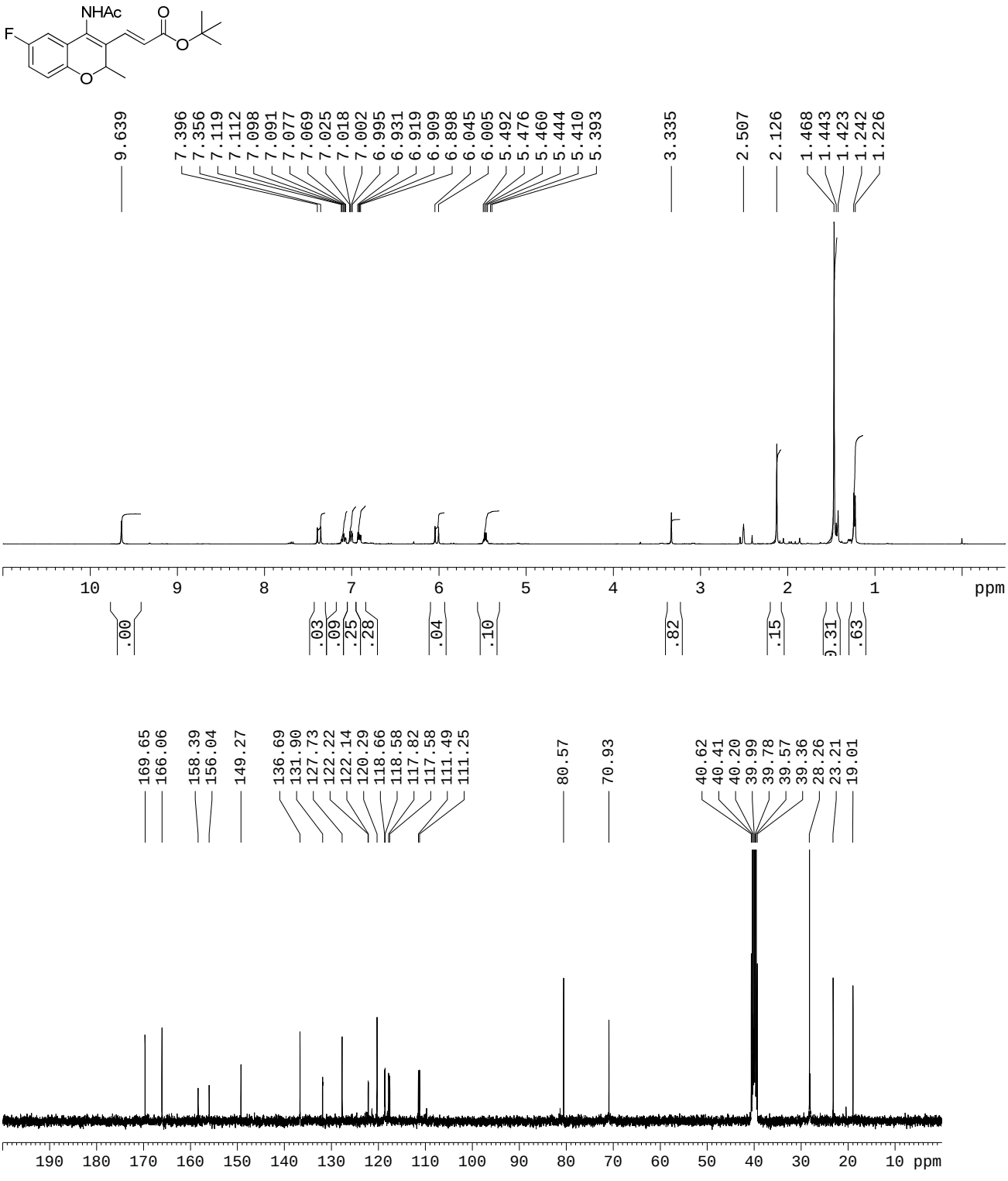
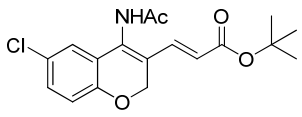
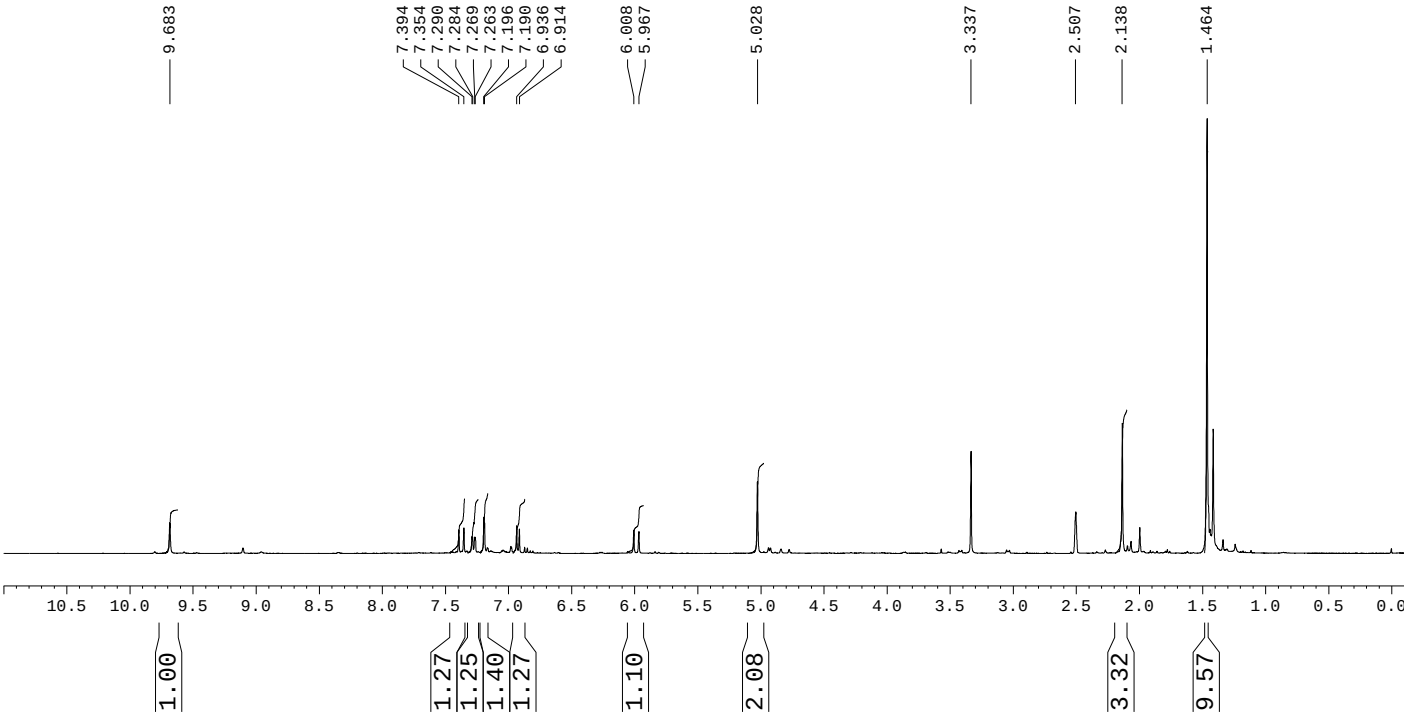
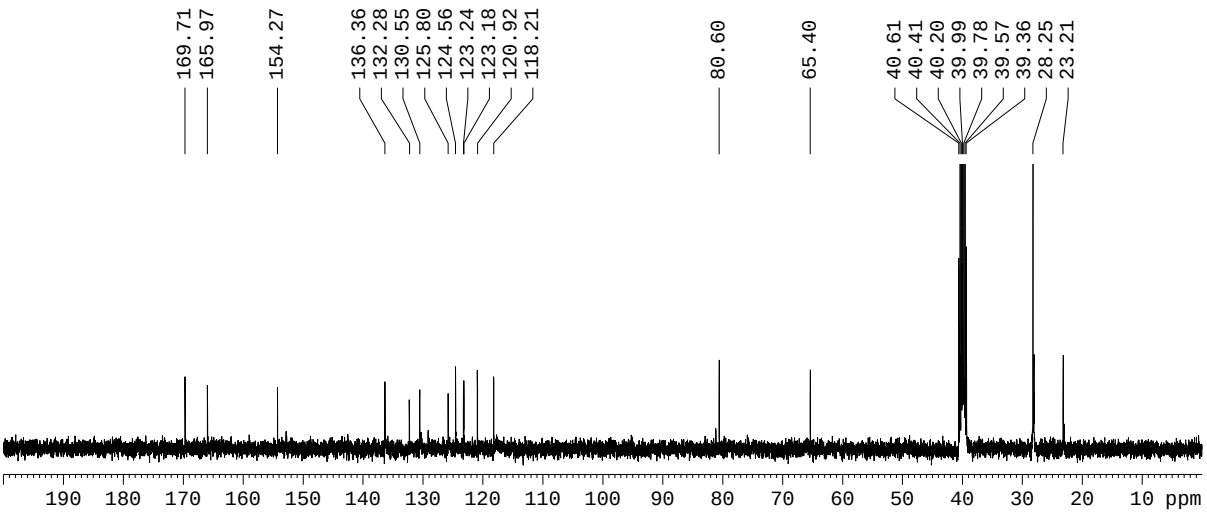
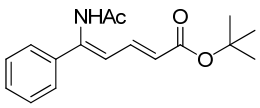
7.371
7.106
7.098
7.085
7.063
7.020
7.013
6.997
6.932
6.920
6.910
6.899
6.012
5.972
4.988
3.338
2.509
2.132
1.463
10
9
8
7
6
5
4
3
2
1
ppm
0.96
1.02
3.19
1.00
1.97
3.06
9.54
169.70
166.01
158.53
156.18
151.71
136.42
132.80
123.33
122.99
122.91
120.81
117.71
117.62
117.49
117.25
111.63
111.38
80.58
65.32
40.61
40.40
40.19
39.98
39.77
39.56
39.35
28.25
23.19
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

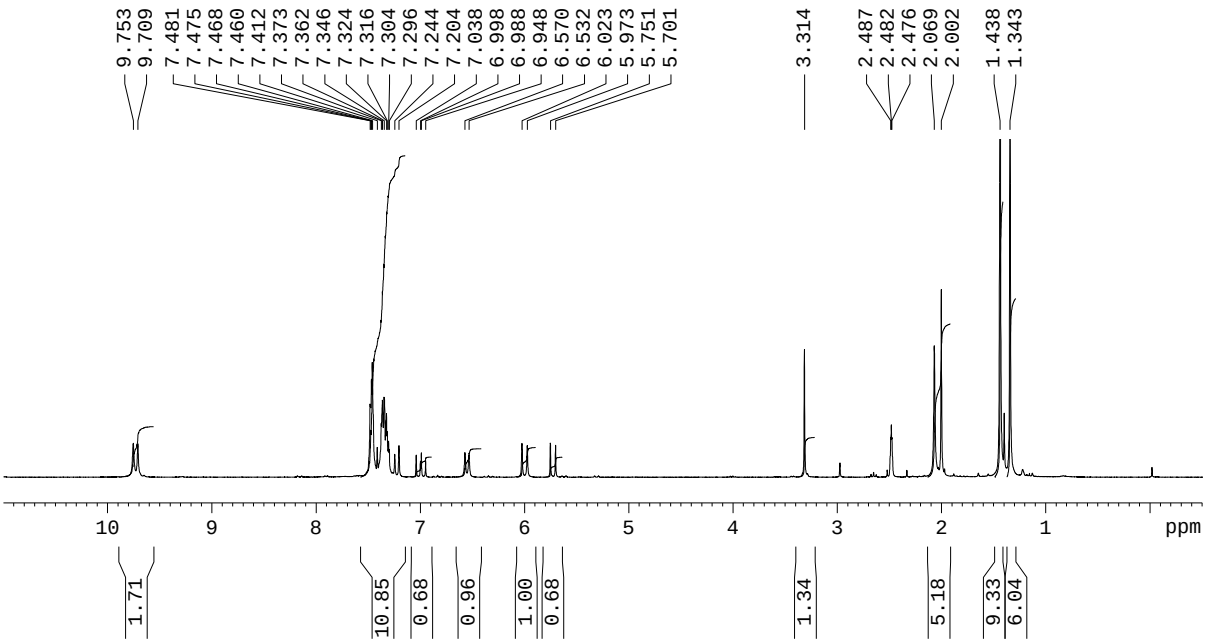









NHAc
O
O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7.460
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7.373
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7.346
7.324
7.316
7.304
7.296
7.244
7.204
7.038
6.998
6.988
6.948
6.570
6.532
6.023
5.973
5.751
5.701
3.314
2.487
2.482
2.476
2.069
2.002
1.438
1.343
10
9
8
7
6
5
4
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2
1
ppm
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10.85
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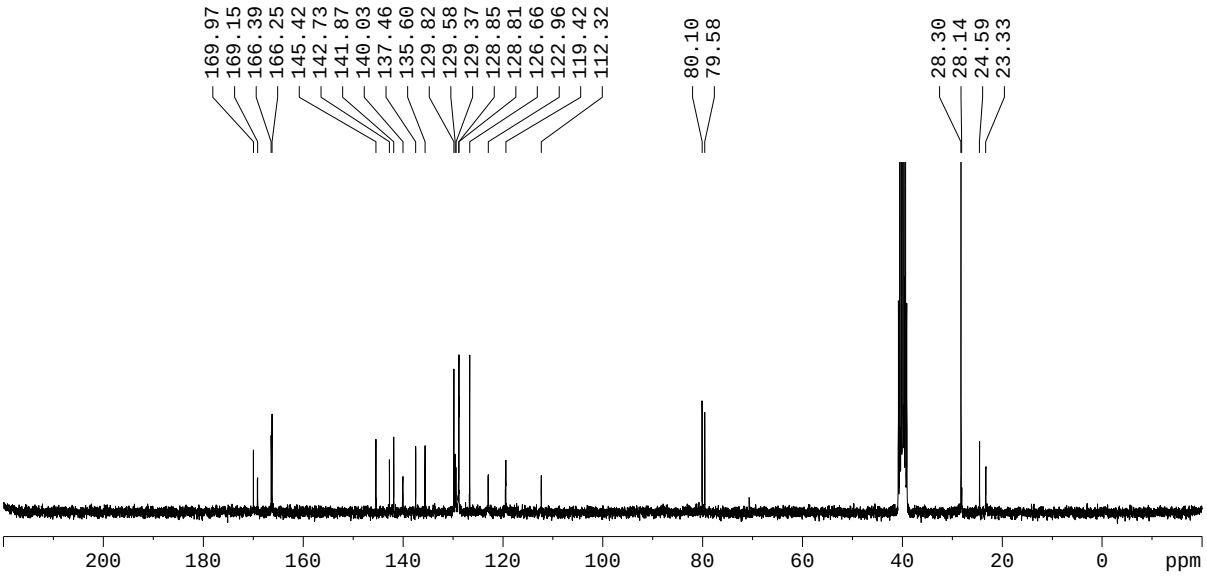
0.96
1.00
0.68
1.34
5.18
9.33
6.04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169.15
166.39
166.25
145.42
142.73
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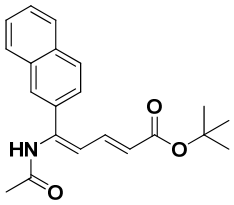
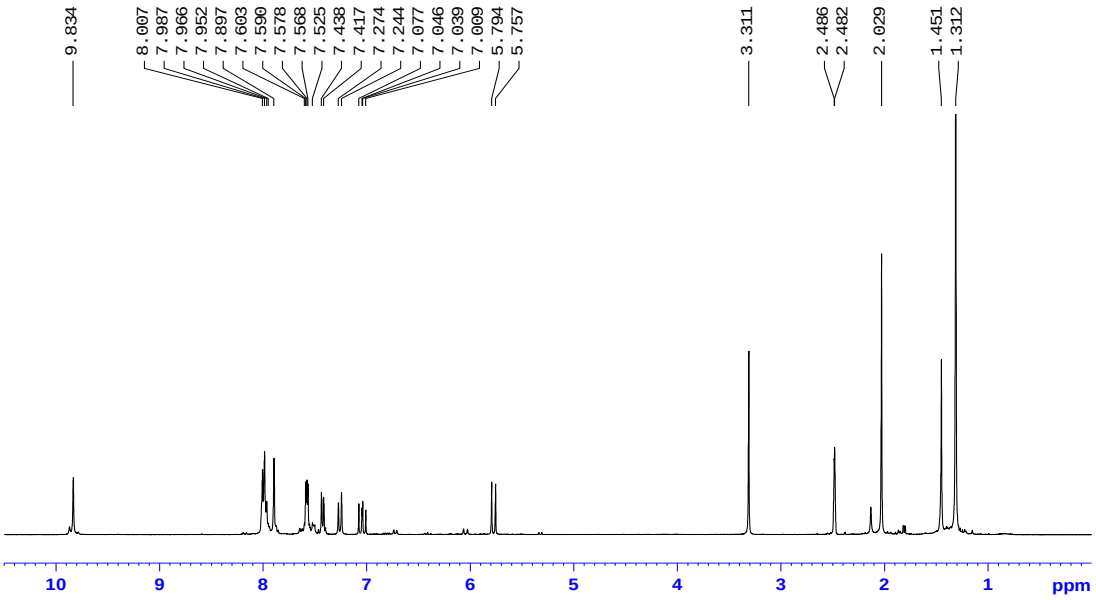
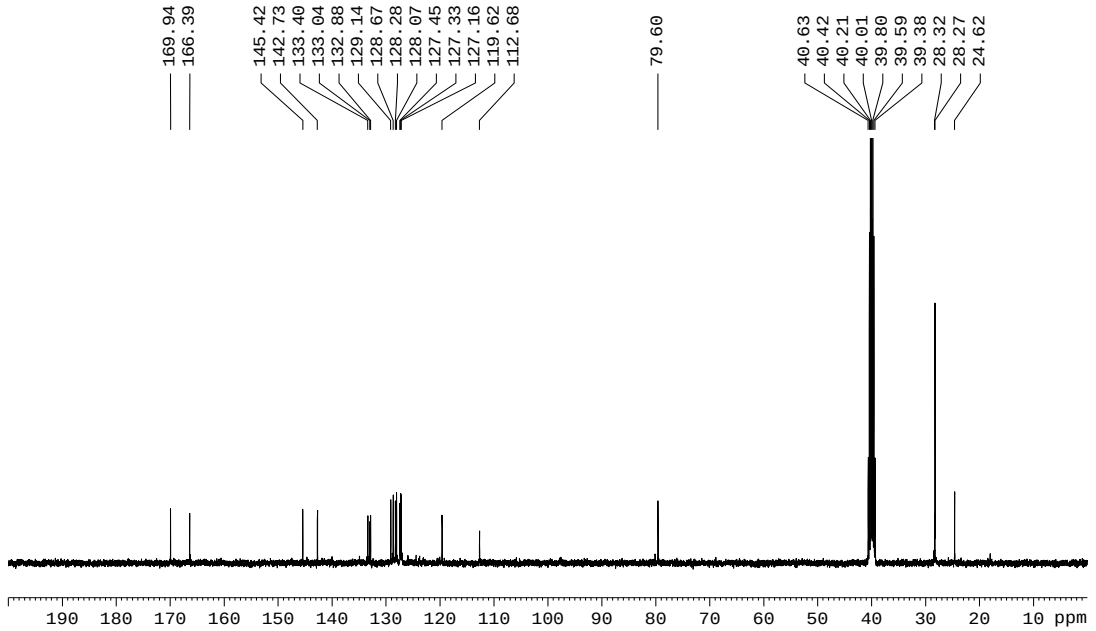
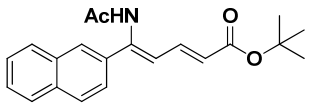
140.03
137.46
135.60
129.82
129.58
129.37
128.85
128.81
126.66
122.96
119.42
112.32
80.10
79.58
28.30
28.14
24.59
23.33
200
180
160
140
120
100
80
60
40
20
0
ppm



(2*E*,4*E*)-*tert*-butyl 5-acetamido-5-(naphthalen-2-yl)penta-2,4-dienoate







(2*E*,4*Z*)-*tert*-butyl 5-acetamido-5-(naphthalen-2-yl)penta-2,4-dienoate